REPLACEMENT NON-TOXIC SEALANTS FOR STANDARD CHROMATED SEALANTS / SERDP Project No. 1075

Alan J. Fletcher
AFRL/MLSA
Materials and Manufacturing Directorate
Air Force Research Laboratory
Systems Support Division
Wright-Patterson AFB, OH 45433-7718

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Alan J Fletcher

MLSA/Materials Integrity Branch
Materials and Manufacturing Directorate
Air Force Research Laboratory
Systems Support Division

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AFRL/MLSA
2179 12th Street
WPAFB, OH 45433-4418

NAVAIR
Polymers & Composites Branch
Polymer Technology Team Lead
Patuxent River, MD

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14. ABSTRACT
Strategic Environmental Research and Development Program (SERDP) 1075, entitled "Replacement Non-Toxic Sealants for Standard Chromated Sealants" was funded by SERDP and carried out from 1999 – 2004. The goal of this program was to develop environmentally compatible, non-chromated, drop-in replacement sealants for military use. In addition to chrome elimination, the volatile organic content (VOC) of the sealants was significantly reduced. These environmental goals are further enhanced by rapid cure times and longer shelf life.

A seven step program was carried out by a team of experts from the Air Force Research Laboratory (AFRL), Naval Air Warfare Center (NAWC), Army Research Laboratory (ARL), Environmental Protection Agency (EPA), Department of Energy (DOE), University of Dayton Research Laboratory (UDRI), and Products Research Corp. (PRC). AFRL was the principle investigator; PRC formulated the sealants; UDRI, NAWC and ARL tested the formulations; EPA provided engineering expertise on low VOC solvents and DOE provided technical support.

A new rapid curing polythioether polymer was used as base. Several epoxy and urethane curing agents were tried and combinations of non-chrome salts were investigated. After a number of prototype formulations were developed and tested, the best formulation was tested and qualified to both military and industry standards. The final phase of the program developed other classes of sealants for a wide range

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EXECUTIVE SUMMARY

Strategic Environmental Research and Development Program (SERDP) 1075, entitled "Replacement Non-Toxic Sealants for Standard Chromated Sealants" was funded by SERDP and carried out from 1999 – 2004. The goal of this program was to develop environmentally compatible, non-chromated, drop-in replacement sealants for military use. In addition to chrome elimination, the volatile organic content (VOC) of the sealants was significantly reduced. These environmental goals are further enhanced by rapid cure times and longer shelf life.

A seven step program was carried out by a team of experts from the Air Force Research Laboratory (AFRL), Naval Air Warfare Center (NAWC), Army Research Laboratory (ARL), Environmental Protection Agency (EPA), Department of Energy (DOE), University of Dayton Research Laboratory (UDRI), and Products Research Corp. (PRC). AFRL was the principle investigator; PRC formulated the sealants; UDRI, NAWC and ARL tested the formulations; EPA provided engineering expertise on low VOC solvents and DOE provided technical support.

A new rapid curing polythioether polymer was used as base. Several epoxy and urethane curing agents were tried and combinations of non-chrome salts were investigated. After a number of prototype formulations were developed and tested, the best formulation was tested and qualified to both military and industry standards. The final phase of the program developed other classes of sealants for a wide range of uses.

The end result of the program is several full qualified and ready for market sealants that eliminate the use of hexavalent chrome, reduce VOCs, increase shelf-life and cure more rapidly than the current sealants.

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SECTION 1
BACKGROUND AND INTRODUCTION

The primary use of sealants is to provide an electrically insulating, corrosion-resistant barrier between dissimilar metals. To accomplish this purpose, the preferred corrosion inhibitors for aerospace sealants in the past have been chrome-containing compounds. For the chrome to be an effective corrosion inhibitor, the oxidation state must be hexavalent. This is the most hazardous form of chrome. In addition, these sealants contain high VOC solvents (toluene and MEK) that are necessary for proper processing and curing.

Chromated corrosion-inhibiting sealants are typically applied to most aircraft faying surfaces. All military aircraft are required to use this type sealant in dry bay areas, wheel wells, cargo bays, radomes, and access panels. Commercial aircraft employ these sealants in the same general areas, but the requirements are less stringent. Sometimes these materials are also used to wet-install fasteners, overcoat fasteners, and fillet-seal seams. In addition to these uses, a minor quantity can be found in weapons systems that are exposed to non-benign environmental situations.

The sealants industry has been researching and developing new chrome replacement products for several years. One new chromate-free, corrosion-inhibiting sealant has been developed, tested, and transitioned to the field. Replacement for only one class of material has been accomplished so far. There are many more types and classes of materials that need to be developed. Recent advances in polymer chemistry have provided ways to develop a drop-in replacement material. This new polymer has some properties that are very beneficial to corrosion-inhibiting sealants, such as rapid cure times without reducing work life, a pleasant odor, excellent rheological properties, cure at low temperature, and high solvent resistance. The work being performed in the effort reported here is directed towards utilizing this new polymer to formulate chrome-free, corrosion-inhibiting sealants for all the types and classes of AMS 3265B sealants.

PRC-DeSoto International, Inc. has developed the new polymer that is being used to formulate these corrosion-inhibiting sealant materials. During the first two years of this effort, a subcontract was issued to PRC-DeSoto International, Inc. to develop base polymers, curing agents, corrosion-inhibiting agents, and prototype sealant formulations suitable for a chrome-free, corrosion-inhibiting sealant system.

Once the best base polymer, curing agent, and corrosion-inhibiting agent were identified, the next task focused on formulating an optimized sealant capable of meeting the requirements of AMS 3265B aerospace sealant specification. To accomplish this goal, the final phase of work has focused on three specific tasks:

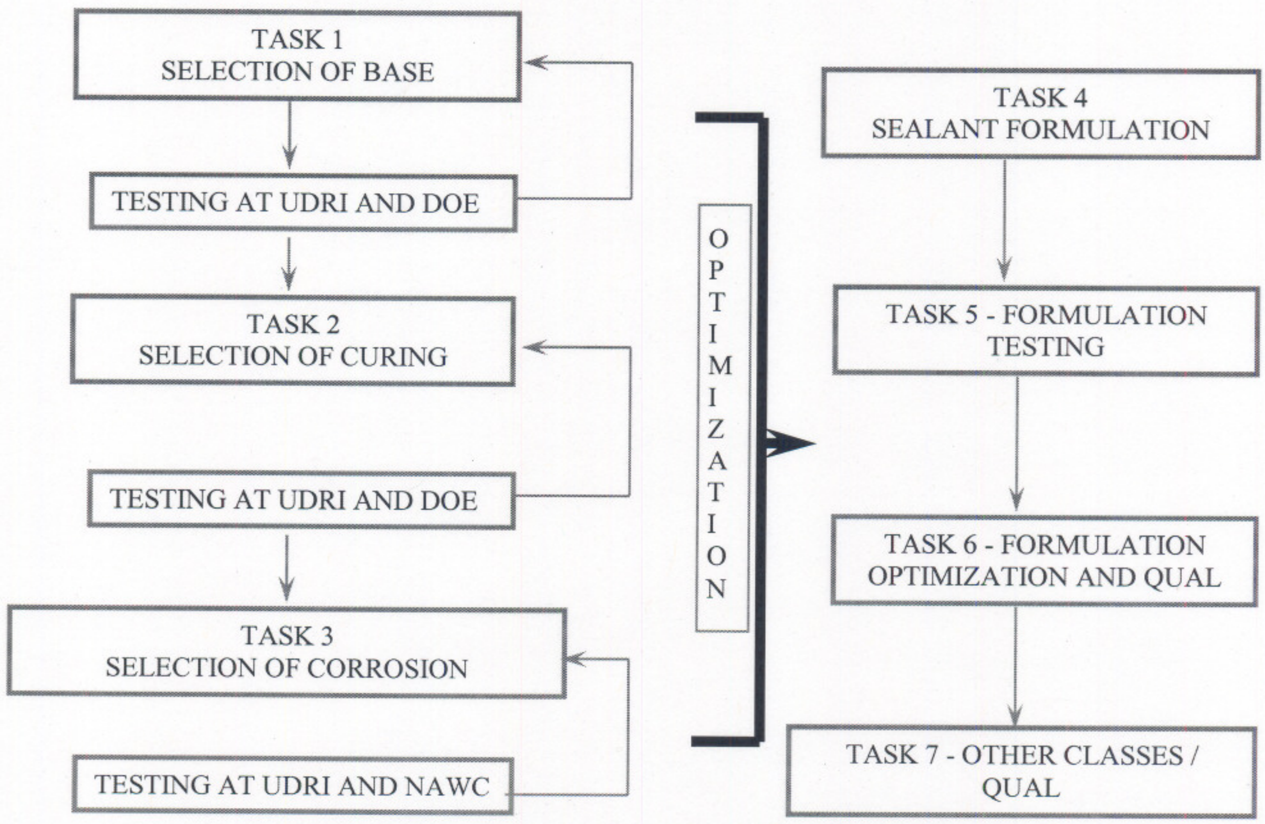
Task 1 – Class B-2 formula optimization
Task 2 – Qualification Testing of Class B-2
Task 3 – Formulation of other classes of sealant

SECTION 2
PROGRAM EXECUTION

A team of experts from Air Force Research Laboratory (AFRL), Naval Air Warfare Center (NAWC), Army Research Laboratory (ARL), Environmental Protection Agency (EPA), Department of Energy (DOE), University of Dayton Research Laboratory (UDRI), and Products Research Corp. (PRC) carried out a seven step program. AFRL was the principle investigator; PRC formulated the sealants; UDRI, NAWC and ARL tested the formulations; EPA provided engineering expertise on low VOC solvents and DOE provided technical support.

Task 1 was to develop a base compound that minimized VOCs and maximized shelf-life. Task 2 was to identify a curing agent that provided sufficient work life and cured as rapidly as possible. Task 3 was to develop a non-chrome leachable additive that function as a corrosion inhibitor and performed at least as well as the hexavalent chrome additive. Task 4 was to develop a prototype sealant based upon eh work in Tasks 1-3. These four tasks were the responsibility of PRC. The work under tasks 1-4 are detailed in Appendix A.

Task 5 was the testing of the prototype. UDRI tested all the physical properties, NAWC and ARL tested the corrosion inhibition properties. Task 6 was formulation optimization by PRC and qualification testing by UDRI and NAWC. UDRI tested the sealants to industry standards and NAWC tested them to military specifications. Task 7 was to develop and test other classes of sealants based on the optimized material. Development was performed by PRC and testing was completed UDRI. The detailed work of Task 5 is covered in Appendix B. A schematic of the tasking is illustrated below.



Other tasks on the program include a study of use report by the US Army Armament Research, Development and Engineering Command (ARDEC) (see Appendix C) and a white paper outlining a solvent substitution program (see Appendix D).

SECTION 3
TEST PROCEDURE

The test procedures that were used to evaluate the chrome-free, corrosion-inhibited sealant materials developed in this program are described and specified in the SAE test method standard AMS 3265B, "Sealing Compound, Polysulfide Rubber, Fuel Resistant, Nonchromated Corrosion Inhibiting For Intermittent Use to 360°F (182°C)." This standard sets requirements for a wide spectrum of material properties and characteristics. Some of these properties and characteristics are related to the application or processability of the material and others are a direct measurement of the material's mechanical or physical properties and resistance to degradation. As sealant formulations for the Class B-2 worklife were developed by PRC-DeSoto International, Inc., they were submitted to UDRI for qualification testing per AMS 3265B. Once the optimum formula was chosen based on the results of this testing, Class B-1/2 and C-12 worklife materials were formulated and are being tested.

In addition to the testing that UDRI conducted, two Department of Defense agencies also performed specialized testing. These agencies were the Naval Air Warfare Center (NAWC) and the Army Research Laboratory (ARL). NAWC performed corrosion testing to the requirements of AMS 3265B for both UDRI and NAWC fabricated specimens, and quality conformance testing to the requirements of MIL-PRF-81733, Performance Specification, Sealing and Coating Compound, Corrosion Inhibitive. ARL conducted ASTM G85 A5 (Prohesion) testing. Corrosion and Prohesion tests were performed at each of these laboratories on the optimized sealant formulation only.

SECTION 4
TEST RESULTS

A total of three Class B-2 formulations, designated RW3758-71, Lot nos. RT0981, RT1002, and RT0946, were submitted sequentially to UDRI for testing to the specification requirements of AMS 3265B. As test failures manifested problems with the formulation, minor changes were incorporated into the sealant package, until the optimized package (Lot no. RT0946) was identified. Full qualification testing was completed for this optimized sealant. Results of this process are shown in Tables 3-1 to 3-11, with Tables 3-4 to 3-11 representing the actual qualification testing results that will be submitted for approval. This optimized formulation was also submitted to the Department of Defense agencies for specialized testing. Results of the AMS 3265B Corrosion testing performed by NAWC are shown in Table 3-12. Results of the ASTM G85 A5 Prohesion testing conducted by ARL are shown in Table 3-13.

Results of the MIL-PRF-81733 quality conformance testing, performed by NAWC, with the optimized formulation of RW3758-71, Class B-2, Lot no. RT0946, are shown in Table 3-14

and 3-15. Results of testing of initial formulations to MIL-PRF-81733 requirements by NAWC are shown in Appendix E.

Three formulations of Class B-1/2 sealant were also submitted to UDRI and NAWC for testing. Results of the qualification testing of RW 3758-71, Class B-1/2, Lot nos. RT0982, RT1001, and RT0960 are shown in Tables 3-16 to 3-24. Again, as test failures identified problems with the formulation, minor changes were made until the optimized package was identified (Lot no. RT0960).

TABLE 3-1
APPLICATION RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0981

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	12700 pse	9000 to 16,000 pse
Viscosity of Accelerator	Std. Cond.	2100 pse	700 to 1600 pse
Flow	Initial	0.1 in.	.10 to .75 inches
	50 mins.	0.05 in.	.10 to .75 inches
	90 mins.	0.1 in.	.10 to .75 inches
Application Time	Std. Cond.	19 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass	24 hrs (max)
Std Cure Time	Std. Cond.	31 pts	30 pts. @ 72 hrs.
14-Day Hardness	Std. Cond.	42 pts	40 pts Shore A (min)
Nonvolatile Content	Std. Cond.	98%	92% (min)

TABLE 3-2
PEEL STRENGTH RESULTS
RW 3758-71, CLASS B-2, LOT NO. RT0981

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
MIL-C-5541 (Alodined Al)	7 days @ 140°F in AMS 2629	19	100	20	100
	7 days @ 140°F in AMS 2629 /SW	33 25	100 100		
	Fuel Cycle (X6)	27 22	100 100		
AMS 2471 (Anodized Al)	7 days @ 140°F in AMS 2629	0	0	20	100
	7 days @ 140°F in AMS 2629 /SW	1 5	0 0		
	Fuel Cycle (X6)	35 0	88 0		
AMS 5516 w/ AMS 3100 (Stainless Steel)	7 days @ 140°F in AMS 2629	0	0	20	100
	7 days @ 140°F in AMS 2629 /SW	33 30	100 100		
	Fuel Cycle (X6)	33 27	100 100		
AMS 4911 w/ AMS 3100 (Titanium)	7 days @ 140°F in AMS 2629	0	0	20	100
	7 days @ 140°F in AMS 2629 /SW	33 31	100 100		
	Fuel Cycle (X6)	33 29	100 100		
	70 days @ 140°F in AMS 2629	7	30		
	70 days @ 140°F in AMS 2629 /SW	28 28	100 100		

TABLE 3-2 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NOs. RT0981

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	12	100	20	100
	7 days @ 140°F in AMS 2629 /SW	29	100		
		25	100		
	Fuel Cycle (X6)	30	100		
		26	100		
	70 days @ 140°F in AMS 2629	13	100		
	70 days @ 140°F in AMS 2629 /SW	23	100		
		25	100		
AMS-C-27725 w/ AMS 3100 (Polyurethane)	7 days @ 140°F in AMS 2629	4	33	20	100
	7 days @ 140°F in AMS 2629 /SW	25	100		
		25	100		
	Fuel Cycle (X6)	27	100		
		22	100		
MIL-PRF-23377 (cured 7 days @ std. cond.) (Epoxy Primer)	7 days @ 140°F in SW	30	100	20	100
MIL-PRF-23377 (cured 2 hrs @ 200°F) (Epoxy Primer)	7 days @ 140°F in SW	30	100	20	100
MIL-PRF-85285 w/ AMS 310010 (Polyurethane)	7 days @ 140°F in SW	32	100	20	100
MIL-PRF-85582 w/ AMS 3100 (Water Based Primer)	7 days @ 140°F in SW	26	100	20	100

TABLE 3-2 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0981

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AS 4/3501-6 (Graphite Epoxy) (Peel Side)	7 days @ 140°F in AMS 2629	24	100	20	100
	7 days @ 140°F in AMS 2629 /SW	39 29	100 100		
	Fuel Cycle (X6)	29 21	100 80		
AS 4/3501-6 (Graphite Epoxy) (Tool Side)	7 days @ 140°F in AMS 2629	14	62	20	100
	7 days @ 140°F in AMS 2629 /SW	33 27	100 100		
	Fuel Cycle (X6)	29 19	100 38		
IM7/5250-4 (BMI) (Peel Side)	7 days @ 140°F in AMS 2629	18	100	20	100
	7 days @ 140°F in AMS 2629 /SW	34 29	100 100		
	Fuel Cycle (X6)	34 26	100 100		
IM7/5250-4 (BMI) (Tool Side)	7 days @ 140°F in AMS 2629	21	100	20	100
	7 days @ 140°F in AMS 2629 /SW	25 30	100 100		
	Fuel Cycle (X6)	33 27	100 100		

TABLE 3-3
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NO. RT1002

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
MIL-C-5541 (Alodined Al)	7 days @ 140°F in AMS 2629	28	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
AMS 2471 (Anodized Al)	7 days @ 140°F in AMS 2629	29	100	20	100
	7 days @ 140°F in AMS 2629 /SW	38 2	100 0		
	Fuel Cycle (X6)				
AMS 5516 (Stainless Steel)	7 days @ 140°F in AMS 2629	31	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
AMS 4911 (Titanium)	7 days @ 140°F in AMS 2629	29	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
	70 days @ 140°F in AMS 2629				
	70 days @ 140°F in AMS 2629 /SW				

TABLE 3-3 (CONT)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NO. RT1002

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	40	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
	70 days @ 140°F in AMS 2629				
	70 days @ 140°F in AMS 2629 /SW				
AMS-C-27725 w/ AMS 3100 (Polyurethane)	7 days @ 140°F in AMS 2629			20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
MIL-PRF-23377 (cured 7 days @ std. cond.) (Epoxy Primer)	7 days @ 140°F in SW			20	100
MIL-PRF-23377 (cured 2 hrs @ 200°F) (Epoxy Primer)	7 days @ 140°F in SW			20	100
MIL-PRF-85285 w/ AMS 310010 (Polyurethane)	7 days @ 140°F in SW			20	100
MIL-PRF-85582 w/ AMS 3100 (Water Based Primer)	7 days @ 140°F in SW			20	100

TABLE 3-3 (CONT)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NO. RT1002

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AS 4/3501-6 (Graphite Epoxy) (Peel Side)	7 days @ 140°F in AMS 2629			20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
AS 4/3501-6 (Graphite Epoxy) (Tool Side)	7 days @ 140°F in AMS 2629	31	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
IM7/5250-4 (BMI) (Peel Side)	7 days @ 140°F in AMS 2629	38	100	20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
IM7/5250-4 (BMI) (Tool Side)	7 days @ 140°F in AMS 2629			20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				

TABLE 3-4
APPLICATION RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	11400 pse	9000 to 16,000 pse
Viscosity of Accelerator	Std. Cond.	1080 pse	700 to 1600 pse
Flow	Initial	0.1 in.	.10 to .75 inches
	50 mins.	0.02 in.	.10 to .75 inches
	90 mins.	0.05 in.	.10 to .75 inches
Application Time	Std. Cond.	15.6 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass	24 hrs (max)
Std Cure Time	Std. Cond.	33 pts	30 pts. @ 72 hrs.

TABLE 3-5
QUICK-FREEZE/QUICK THAW RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Test	Conditioning	Test Results	Specification Requirements
Nonvolatile Content	7 days @ 158°F	98%	92% (min)
Flow	Initial	0.1 in.	.10 to .75 inches
	50 mins.	0.1 in.	.10 to .75 inches
	90 mins.	0.1 in.	.10 to .75 inches
Application Time	Std. Cond.	4.8 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass	24 hrs (max)
Std Cure Time	Std. Cond.	34 pts	30 pts. @ 72 hrs.

TABLE 3-6
PERFORMANCE RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Test	Conditioning	Test Results	Specification Requirements
Specific Gravity	Std. Cond.	1.55	1.50 (max.)
14-Day Hardness	Std. Cond.	46	40 pts Shore A (min.)
Shaving and Sanding	Std. Cond.	Pass	No rolling or tearing of sealant, smooth finish
Air Content	Std. Cond.	2.10%	4% (max.)
Weight Loss & Flexibility	7 days @ 140°F in AMS 2629 + 24 hrs @ 120°F in Air + Std. Cond. in desiccator	2.40% Pass	10% (wt max.) No cracking or checking
Resistance to Thermal Rupture	Control	Pass	No blistering or sponging and less than 0.15 in. deformation
	120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629	Pass	
Low Temperature Flexibility	Control	Pass	No cracking, checking or loss of adhesion
	120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629 + Heat Cycle	Pass	
Hydrolytic Stability	120 days @ 160°F/95% RH + 14 days @ Std. Cond.	45 pts	30 pts Shore A (min.)
Paintability	24 hrs in distilled H_2O	Pass	No separation from sealant
Weathering	30 days @ 140°F cycling	Fail	No cracking, chalking, peeling or loss of adhesion
Volume Swell	Std. Cond.	12.90%	5 to 15 %

TABLE 3-7
TENSILE STRENGTH AND ELONGATION
RW3758-71, CLASS B-2, LOT NO. RT0946

Conditioning	Test Results		Specification Requirements	
	Tensile Strength (psi)	Elongation (%)	Tensile Strength (psi)	Elongation (%)
Std. Cure	367	281	200	200
12 days @ 140°F in AMS 2629	406	150	200	200
120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629	418	160	125	100
120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629 + Heat Cycle	287	68	125	25
Standard Heat Cycle	239	101	200	100
72 hrs @ std. cond. in AMS 3021	412	239	200	200
72 hrs @ std. cond. in AMS 3020	383	241	200	200

TABLE 3-8
PEEL STRENGTH RESULTS
RW 3758-71, CLASS B-2, LOT NO. RT0946

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
MIL-C-5541 (Alodined Al)	7 days @ 140°F in AMS 2629	41	100	20	100
	7 days @ 140°F in AMS 2629 /SW	51 40	100 100		
	Fuel Cycle (X6)	39 31	100 79		
AMS 2471 (Anodized Al)	7 days @ 140°F in AMS 2629	47	100	20	100
	7 days @ 140°F in AMS 2629 /SW	46 36	100 100		
	Fuel Cycle (X6)	32 5	100 0		
AMS 5516 w/ AMS 3100 (Stainless Steel)	7 days @ 140°F in AMS 2629	45	100	20	100
	7 days @ 140°F in AMS 2629 /SW	44 38	100 100		
	Fuel Cycle (X6)	42 33	100 100		
AMS 4911 w/ AMS 3100 (Titanium)	7 days @ 140°F in AMS 2629	39	100	20	100
	7 days @ 140°F in AMS 2629 /SW	50 40	100 100		
	Fuel Cycle (X6)	41 30	100 100		
	70 days @ 140°F in AMS 2629	28	100		
	70 days @ 140°F in AMS 2629 /SW	41 39	100 100		

TABLE 3-8 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NOs. RT0946

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	41	100	20	100
	7 days @ 140°F in AMS 2629 /SW	44	100		
		34	100		
	Fuel Cycle (X6)	36	100		
		31	100		
	70 days @ 140°F in AMS 2629	26	100		
	70 days @ 140°F in AMS 2629 /SW	38	100		
		32	100		
AMS-C-27725 w/ AMS 3100 (Polyurethane)	7 days @ 140°F in AMS 2629	44	100	20	100
	7 days @ 140°F in AMS 2629 /SW	55	100		
		38	100		
	Fuel Cycle (X6)	39	100		
		31	100		
MIL-PRF-23377 (cured 7 days @ std. cond.) (Epoxy Primer)	7 days @ 140°F in SW	45	100	20	100
MIL-PRF-23377 (cured 2 hrs @ 200°F) (Epoxy Primer)	7 days @ 140°F in SW	46	100	20	100
MIL-PRF-85285 w/ AMS 310010 (Polyurethane)	7 days @ 140°F in SW	40	100	20	100
MIL-PRF-85582 w/ AMS 3100 (Water Based Primer)	7 days @ 140°F in SW	42	100	20	100

TABLE 3-8 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AS 4/3501-6 (Graphite Epoxy) (Peel Side)	7 days @ 140°F in AMS 2629	35	100	20	100
	7 days @ 140°F in AMS 2629 /SW	40 39	100 100		
	Fuel Cycle (X6)	35 33	100 100		
AS 4/3501-6 (Graphite Epoxy) (Tool Side)	7 days @ 140°F in AMS 2629	37	100	20	100
	7 days @ 140°F in AMS 2629 /SW	42 36	100 100		
	Fuel Cycle (X6)	31 30	100 100		
IM7/5250-4 (BMI) (Peel Side)	7 days @ 140°F in AMS 2629	39	100	20	100
	7 days @ 140°F in AMS 2629 /SW	50 42	100 100		
	Fuel Cycle (X6)	38 29	100 100		
IM7/5250-4 (BMI) (Tool Side)	7 days @ 140°F in AMS 2629	41	100	20	100
	7 days @ 140°F in AMS 2629 /SW	48 36	100 100		
	Fuel Cycle (X6)	43 26	100 100		

TABLE 3-9
REPAIRABILITY RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
To Self	Control	42	100	10	100
	Conditioned	34	100		
To AMS 3265 (PR-1775 B-2)	Control	32	100	10	100
	Conditioned	31	100		
To AMS 3276 (PR-1750 B-2)	Control	56	100	10	100
	Conditioned	42	100		

TABLE 3-10
ACCELERATED STORAGE RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	8200 pse	9000 to 16000 pse
Flow	Initial	0.6	.10 to .75 inches
	50 mins.	0.2	.10 to .75 inches
	90 mins.	0.2	.10 to .75 inches
Application Time	Std. Cond.	25 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass @ 22 hrs	24 hrs (max)
Std Cure Time	Std. Cond.	24 pts	30 pts. @ 72 hrs.
Peel Strength (AMS-C-27725) (Polyurethane)	7 days @ 140°F in AMS 2629	36 lbs/100%	20 lbs/in 100% Cohesive
	7 days @ 140°F in AMS 2629/ SW	52 lbs/100% 36 lbs/100%	

TABLE 3-11
LONG-TERM STORAGE RESULTS
RW3758-71, CLASS B-2, LOT NO. RT0946

Test	Conditioning	Test Results	Specification Requirements
Application Time	Std. Cond.	6.3 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass @ 20 hrs	24 hrs (max)
Std Cure Time	Std. Cond.	19 pts	30 pts. @ 72 hrs.

TABLE 3-12
CORROSION TEST RESULTS
FOR RW-3758-71, CLASS B-2, LOT NO. RT0946
SUBMITTED TO NAWC

Sample #	4X6 panel	2X3 panel	Comments
NAVAIR			
1	Ti	Al	No corrosion
2	Ti	Al	No corrosion
3	Al	Ti	No corrosion
4	Al	Ti	No corrosion
5	Al	Mg	No corrosion
6	Al	Mg	No corrosion
UDRI			
U1	Al	Ti	Slight discoloration on edges
U2	Al	Comp	Slight discoloration on edges
U3	Al	Comp	Very slight discoloration on edges
U4	Al	Mg	Discolored around fasteners
U5	Al	Ti	Slight discoloration on edges
U6	Al	Mg	Slight discoloration on edges+ fasteners

TABLE 3-13
PROHESION TEST RESULTS
FOR RW-3758-71, CLASS B-2, LOT NO. RT-0946
SUBMITTED TO ARL

Material	Time Conditioned (Weeks)	Gap Width	Adhesion[1]	Evaluations % Corrosion in Scribe	Procedure A[2]	Procedure B[2]
RW-3758-71	1	3 mm	Little, Little	5, 5	10, 10	3*, 10
Req. 1290B	2	3 mm	Good, Good	5, 20	10, 10	10, 10
8-7-03	3	3 mm	Good, Good	5, 10	10, 10	10, 10
	4	3 mm	Good, Good	5, 5	10, 10	10, 10
	5	3 mm	Good, Good	50, 60	10, 7	10, 10
	6	3 mm	Good, Good	90, 80	10, 8	10, 10
	1	5 mm	Little, Little	0, 5	10, 10	10, 4*
	2	5 mm	Good, Good	5, 15	10, 10	10, 10
	3	5 mm	Good, Good	5, 5	10, 10	10, 10
	4	5 mm	Good, Good	5, 10	10, 10	10, 10
	5	5 mm	Good, Good	40, 20	10, 8	10, 10
	6	5 mm	Good, Good	70, 70	8, 8	10, 10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table I (ASTM D 1654) Procedure A Corrosion under coating @ scribe mark; Procedure B Corrosion under unscribed coating
* Moisture Intrusion from Panel Edges causing Discoloration

TABLE 3-14
PHYSICAL AND APPLICATION PROPERTY
TEST RESULTS PER MIL-PRF-81733
FOR RW-3758-71, CLASS B-2, LOT NO. RT-0946
SUBMITTED TO NAWC

TEST PARAMETER	REQUIREMENT	RESULT
Specific gravity, max.	1.5	1.59
Hardness (Shore A)	35, min. (after 14-day cure)	59
Non-Volatile Content, min.	92%	98%
Application Time, at 2 hours	>15g/min	12 g/min
Tack Free Time, max.	12 hours	22 hrs
Tensile/Elongation	250psi/250% elong.	460psi/131% elong.

TABLE 3-15
PEEL STRENGTH PROPERTY
TEST RESULTS PER MIL-PRF-81733
FOR RW-3758-71, CLASS B-2, LOT NO. RT-0946
SUBMITTED TO NAWC

PEEL STRENGTH	REQUIREMENT	RESULT (psiw/failure type)
23377 on Anodized Al	15/100% cohesive	43/100% cohesive
@ 48Hr 83282	15/100% cohesive	23/100% cohesive
@ 48Hr 23699	15/100% cohesive	21/100% cohesive
@ 48Hr JRF	15/100% cohesive	21/100% cohesive
@ 48Hr 3% SaltWater	15/100% cohesive	50/100% cohesive
IM6/3501-6	15/100% cohesive	40/100% cohesive
@ 48Hr 83282	15/100% cohesive	34/100% cohesive
@ 48Hr 23699	15/100% cohesive	22/100% cohesive
@ 48Hr JRF	15/100% cohesive	24/100% cohesive
@ 48Hr 3% SaltWater	15/100% cohesive	31/100% cohesive
Alodined Al	15/100% cohesive	42/100% cohesive
@ 48Hr 83282	15/100% cohesive	35/100% cohesive
@ 48Hr 23699	15/100% cohesive	31/100% cohesive
@ 48Hr JRF	15/100% cohesive	20/100% cohesive
@ 48Hr 3% SaltWater	15/100% cohesive	36/100% cohesive
Titanium	15/100% cohesive	31/50% adhesive
@ 48Hr 83282	15/100% cohesive	35/100% cohesive
@ 48Hr 23699	15/100% cohesive	30/40% adhesive
@ 48Hr JRF	15/100% cohesive	27/100% cohesive
@ 48Hr 3% SaltWater	15/100% cohesive	

TABLE 3-16
APPLICATION RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT0982

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	9000 pse	9000 to 16,000 pse
Viscosity of Accelerator	Std. Cond.	2100 pse	700 to 1600 pse
Flow	Initial	0.12 in.	.10 to .75 inches
Application Time	Std. Cond.	74 gms/min	15 gms/min @ 1/2 hrs
Tack-Free Time	Std. Cond.	Pass	12 hrs (max)
Std Cure Time	Std. Cond.	25 pts	30 pts. @ 32 hrs.
Nonvolatile Content	Std. Cond.	98%	92% (min)
14-Day Hardness	Std. Cond.	60 pts	40 pts Shore A (min)
Peel Strength AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	17 lbs/ 10%	20 lbs/ 100% Coh.

TABLE 3-17
APPLICATION RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT1001

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	7000 pse	9000 to 16,000 pse
Viscosity of Accelerator	Std. Cond.	1500 pse	700 to 1600 pse
Flow	Initial	0.3 in.	.10 to .75 inches
Application Time	Std. Cond.	120 gms/min	15 gms/min @ 1/2 hrs
Tack-Free Time	Std. Cond.	Pass @ 5.5 hrs	12 hrs (max)
Std Cure Time	Std. Cond.	32 pts @ 9.5 hrs	30 pts. @ 32 hrs.
Nonvolatile Content	Std. Cond.	98%	92% (min)

TABLE 3-18
PERFORMANCE RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT1001

Test	Conditioning	Test Results	Specification Requirements
Specific Gravity	Std. Cond.	1.54	1.50 (max.)
14-Day Hardness	Std. Cond.	57	40 pts Shore A (min.)
Shaving and Sanding	Std. Cond.	Pass	No rolling or tearing of sealant, smooth finish
Air Content	Std. Cond.	0.90%	4% (max.)
Weight Loss & Flexibility	7 days @ 140°F in AMS 2629 + 24 hrs @ 120°F in Air + Std. Cond. in desiccator	3.50% Pass	10% (wt max.) No cracking or checking
Resistance to Thermal Rupture	Control	Pass	No blistering or sponging and less than 0.15 in. deformation
	120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629	Pass	
Low Temperature Flexibility	Control	Pass	No cracking, checking or loss of adhesion
	120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629 + Heat Cycle	Pass	
Hydrolytic Stability	120 days @ 160°F/95% RH + 14 days @ Std. Cond.		30 pts Shore A (min.)
Paintability	24 hrs in distilled H_2O	Pass	No separation from sealant
Weathering	30 days @ 140°F cycling	Fail	No cracking, chalking, peeling or loss of adhesion
Volume Swell	Std. Cond.	11.40%	5 to 15 %

TABLE 3-19
TENSILE STRENGTH AND ELONGATION
RW3758-71, CLASS B-1/2, LOT NO. RT1001

Conditioning	Test Results		Specification Requirements	
	Tensile Strength (psi)	Elongation (%)	Tensile Strength (psi)	Elongation (%)
Std. Cure	483	195	200	200
12 days @ 140°F in AMS 2629	303	232	200	200
120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629	357	222	125	100
120 hrs @ 140°F in AMS 2629 + 60 hrs @ 160°F in AMS 2629 + 6 hrs @ 180°F in AMS 2629 + Heat Cycle	247	100	125	25
Standard Heat Cycle	294	130	200	100
72 hrs @ std. cond. in AMS 3021	539	164	200	200
72 hrs @ std. cond. in AMS 3020	464	229	200	200

TABLE 3-20
PEEL STRENGTH RESULTS
RW 3758-71, CLASS B-1/2, LOT NO. RT1001

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
MIL-C-5541 (Alodined Al)	7 days @ 140°F in AMS 2629	51	100	20	100
	7 days @ 140°F in AMS 2629 /SW	20 4	0 0		
	Fuel Cycle (X6)				
AMS 2471 (Anodized Al)	7 days @ 140°F in AMS 2629	51	100	20	100
	7 days @ 140°F in AMS 2629 /SW	11 3	13 0		
	Fuel Cycle (X6)				
AMS 5516 w/ AMS 3100 (Stainless Steel)	7 days @ 140°F in AMS 2629	36	55	20	100
	7 days @ 140°F in AMS 2629 /SW	5 2	0 0		
	Fuel Cycle (X6)				
AMS 4911 w/ AMS 3100 (Titanium)	7 days @ 140°F in AMS 2629	32	63	20	100
	7 days @ 140°F in AMS 2629 /SW	12 3	0 0		
	Fuel Cycle (X6)				
	70 days @ 140°F in AMS 2629				
	70 days @ 140°F in AMS 2629 /SW				

TABLE 3-20 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-1/2, LOT NOs. RT1001

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	62	100	20	100
	7 days @ 140°F in AMS 2629 /SW	67 68	100 100		
	Fuel Cycle (X6)				
	70 days @ 140°F in AMS 2629				
	70 days @ 140°F in AMS 2629 /SW				
AMS-C-27725 w/ AMS 3100 (Polyurethane)	7 days @ 140°F in AMS 2629			20	100
	7 days @ 140°F in AMS 2629 /SW				
	Fuel Cycle (X6)				
MIL-PRF-23377 (cured 7 days @ std. cond.) (Epoxy Primer)	7 days @ 140°F in SW	0	0	20	100
MIL-PRF-23377 (cured 2 hrs @ 200°F) (Epoxy Primer)	7 days @ 140°F in SW	0	0	20	100
MIL-PRF-85285 w/ AMS 310010 (Polyurethane)	7 days @ 140°F in SW	0	0	20	100
MIL-PRF-85582 w/ AMS 3100 (Water Based Primer)	7 days @ 140°F in SW	6	0	20	100

TABLE 3-20 (CONT.)
PEEL STRENGTH RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT1001

Adherend	Conditioning	Test Results		Specification Requirements	
		Load (lbs/in)	% Cohesion	Load (lbs/in)	% Cohesion
AS 4/3501-6 (Graphite Epoxy) (Peel Side)	7 days @ 140°F in AMS 2629	56	100	20	100
	7 days @ 140°F in AMS 2629 /SW	16 27	3 36		
	Fuel Cycle (X6)				
AS 4/3501-6 (Graphite Epoxy) (Tool Side)	7 days @ 140°F in AMS 2629	42	80	20	100
	7 days @ 140°F in AMS 2629 /SW	0 0	0 0		
	Fuel Cycle (X6)				
IM7/5250-4 (BMI) (Peel Side)	7 days @ 140°F in AMS 2629	54	100	20	100
	7 days @ 140°F in AMS 2629 /SW	6 3	0 0		
	Fuel Cycle (X6)				
IM7/5250-4 (BMI) (Tool Side)	7 days @ 140°F in AMS 2629	34	60	20	100
	7 days @ 140°F in AMS 2629 /SW	8 6	0 0		
	Fuel Cycle (X6)				

TABLE 3-21
ACCELERATED STORAGE RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT1001

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	6100 pse	9000 to 16000 pse
Flow	Initial	0.75 in.	.10 to .75 inches
Application Time	Std. Cond.	213 gms/min	15 gms/min @ 2 hrs
Tack-Free Time	Std. Cond.	Pass @ 5 hrs	24 hrs (max)
Std Cure Time	Std. Cond.	30 pts @ 25 hrs	30 pts. @ 72 hrs.
Peel Strength (AMS-C-27725) (Polyurethane)	7 days @ 140°F in AMS 2629		20 lbs/in 100% Cohesive
	7 days @ 140°F in AMS 2629/ SW		

TABLE 3-22
APPLICATION RESULTS
RW3758-71, CLASS B-1/2, LOT NO. RT0960

Test	Conditioning	Test Results	Specification Requirements
Viscosity of Base	Std. Cond.	8300 pse	9000 to 16,000 pse
Viscosity of Accelerator	Std. Cond.	1300 pse	700 to 1600 pse
Nonvolatile Content	7 days @ 158°F	97%	92% (min)
Flow	Initial	0.4 in.	.10 to .75 inches
Application Time	Std. Cond.	170 gms/min.	15 gms/min @ 1/2 hrs
Tack-Free Time	Std. Cond.	Pass @ 6.5 hrs	12 hrs (max)
Std Cure Time	Std. Cond.	25 pts @ 32 hrs.	30 pts. @ 32 hrs.
14-Day Hardness	Std. Cond.	50 pts	40 pts Shore A (min)
Peel Strength AMS-C-27725 (Polyurethane)	7 days @ 140°F in AMS 2629	72 lbs/ 100%	20 lbs/ 100% Coh.

TABLE 3-23
PHYSICAL AND APPLICATION PROPERTY
TEST RESULTS PER MIL-PRF-81733
FOR RW-3758-71, CLASS B-1/2, LOT NO. RT-0960
SUBMITTED TO NAWC

TEST PARAMETER	REQUIREMENT	RESULT
Specific gravity, max.	1.5	1.57
Hardness (Shore A)	35, min. (after 14-day cure)	77
Non-Volatile Content, min.	92%	98
Application Time, at 1/2 hours	>15g/min	149 g/min
Tack Free Time, max.	2 hours	3 hrs
Tensile/Elongation	250psi/250% elong.	538psi/121% elong.

TABLE 3-24
PEEL STRENGTH PROPERTY
TEST RESULTS PER MIL-PRF-81733
FOR RW-3758-71, CLASS B-1/2, LOT NO. RT-0960
SUBMITTED TO NAWC

PEEL STRENGTH	REQUIREMENT	RESULT (psiw/failure type)
23377 on Anodized Al	20/100% cohesive	43/100% cohesive
@ 48Hr 83282	20/100% cohesive	35/100% cohesive
@ 48Hr 23699	20/100% cohesive	28/100% cohesive
@ 48Hr JRF	20/100% cohesive	22/100% cohesive
@ 48Hr 3% SaltWater	20/100% cohesive	0/100% adhesive
IM6/3501-6	20/100% cohesive	40/100% cohesive
@ 48Hr 83282	20/100% cohesive	46/100% cohesive
@ 48Hr 23699	20/100% cohesive	42/100% cohesive
@ 48Hr JRF	20/100% cohesive	30/30% adhesive
@ 48Hr 3% SaltWater	20/100% cohesive	41/20% adhesive
Alodined Al	20/100% cohesive	39/100% cohesive
@ 48Hr 83282	20/100% cohesive	33/100% cohesive
@ 48Hr 23699	20/100% cohesive	35/100% cohesive
@ 48Hr JRF	20/100% cohesive	28/100% cohesive
@ 48Hr 3% SaltWater	20/100% cohesive	56/20% adhesive
Titanium	20/100% cohesive	21/85% adhesive
@ 48Hr 83282	20/100% cohesive	32/28% adhesive
@ 48Hr 23699	20/100% cohesive	28/35% adhesive
@ 48Hr JRF	20/100% cohesive	49/100% cohesive
@ 48Hr 3% SaltWater	20/100% cohesive	58/100% cohesive

SECTION 5
CONCLUSIONS

The development of a chrome-free corrosion inhibiting sealant that meets the specification requirements of AMS 3265B was successfully accomplished in this program. An optimized Class B-2 worklife of the sealant compound designated RW3758-71, Lot no. RT0946, completed qualification testing and is ready for field use per approval. In tests at the Department of Defense sites, this material exhibited superior corrosion inhibiting properties. In qualification testing at UDRI it proved to be able to withstand fluid exposures while maintaining high strength and excellent adhesion to typical panel substrates. The material will be provided by the manufacturer with an adhesion promoter package.

The optimized Class B-1/2 sealant identified as RW3758-71, Lot no. RT0960, completed quality conformance testing and is also ready to transition to the field per approval. A Class C-12 worklife of the sealant compound has been formulated and is ready to undergo qualification testing upon arrival at UDRI.

APPENDIX A

PRODUCTS RESEARCH AND DEVELOPMENT (PRC) REPORT

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
300 College Park • Dayton Ohio 45469-0130
937.229.2517 • FAX 937.229.2503

February 20, 2001

REPLACEMENT NON-TOXIC SEALANTS FOR STANDARD CHROMATED SEALANTS, SERDP PROJECT NO. 1075

UDR-TR-2001-00015

FY00 Annual Report

Prepared for:

Chuck Pellerin
SERDP & ESTCP Program Office
901 N. Stuart Street, Suite 303
Arlington, VA 22203

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FOREWARD

This document covers work performed on SERDP Project No. 1075, Replacement Non-Toxic Sealants for Standard Chromated Sealants. It covers Tasks 1-4 of the subject program. The report was prepared by PRC-DeSoto International Inc. in fulfillment of their work on subcontract number RSC99023 with the University of Dayton Research Institute. The majority of the work was carried out at the PRC-DeSoto International's Research and Technology Center in Burbank, California between July 1, 1999 and August 1, 2000.

The project director is Mr. Alan Fletcher (AFRL/MLSA) of WPAFB, Ohio. The project team consists of the Air Force Research Laboratory, the University of Dayton Research Institute (UDRI), PRC-DeSoto International Inc., the Army Research, Development, and Engineering Center (ARDEC), the Army Research Laboratory (ARL), the Naval Air Warfare Center (NAWC), the Department of Energy-Sandia National Laboratories, and the Environmental Protection Agency (EPA).

The primary effort reported here was the development of a base compound, a curing agent, a corrosion inhibiting agent, and a prototype sealant formulation. As the work progressed, samples of each of these components were submitted to other program participants for screening tests. The results of the screening tests were used by PRC-DeSoto to identify the most promising candidates. At the conclusion of Task 4, samples of the formulated sealant were submitted to program participants for evaluation.

OBJECTIVE

The overall objective of this project was to develop a non-chromate containing, corrosion-inhibiting, polythioether-based sealant to replace other, chromate-containing sealants.

PRC-DeSoto International has patented a new class of polythioether polymers, the Permapol® P-3.1 family. These materials provide wide formulating latitude along with the desirable qualities of standard polythioethers (Permapol® P-3) and so are good choices for use in developing a new, non-chromate containing sealant.

PRC-DeSoto International has also patented non-chromate corrosion-inhibitor packages which are ideal candidates for such a sealant. Under the first year of this contract, PRC-DeSoto International agreed to identify and develop Permapol P-3.1 type polymers for use in a non-chromate, corrosion-inhibiting sealant system. PRC-DeSoto International also agreed to identify and develop appropriate curing agents and non-chromate corrosion inhibitor packages, as well as to provide a prototype sealant formulation.

PROJECT OUTLINE (TASKS)

Task 1: Development of a Base Compound
Task 2: Development of Curing Agent
Task 3: Development of Corrosion-inhibiting Agent
Task 4: Development of Prototype Sealant Formulation

TASK 1. DEVELOPMENT OF A BASE COMPOUND

The goal of this task was to identify and develop three polymers suitable for non-chromate-containing, corrosion-inhibiting sealants. Although not every application for such a sealant may require fuel resistance, a number of them do. In order to use the system developed under this project for the maximum number of potential applications, we purposely selected for fuel resistance, as this property is not otherwise easily achieved.

The Permapol P-3.1 family of polythioethers is described in U.S. Patent 5,912,319 (Zook, et. al). The basic synthetic scheme is the reaction of divinylethers with dithiols using various functionalizing agents. Such polymers can be produced with substantially less hazardous waste than standard polythioethers (Permapol® P-3) or polysulfides. The polymers have good formulating latitude due to their structure and low viscosity, making them ideal candidates for this contract.

A large number of polymers were previously screened for potential use in fuel-resistant sealants. Polymers were made with a variety of different monomers in the backbone. Each monomer imparts different properties, such as low temperature flexibility or fluid resistance. A portion of this information is found in Table 1 (next page), which contains information on 2100 MW, 2.1 functional polymers made with different monomers in the backbone. Consult Appendix 1 for a list of abbreviations used throughout this paper.

The information presented in Table 1 includes physical properties of the polymer (such as viscosity and glass transition temperature) and physical properties of the cured polymers (hardness and % weight gain after one week in JRF Type 1 at 140°F). The polymers were cured with a stoichiometric amount of a standard PRC-DeSoto International accelerator based on a blend of Bis A DGE and a Bis F novolac. In this initial study, the glass transition temperature, T_g, was reported as the "take-off point" as opposed to the inflection point; the inflection point would be about 5 °C higher.

The best candidates would have low viscosity (for ease of formulation), hardness between about 20 and 50 Shore A, low weight gain in fuel (for good fuel resistance), and low T_g (for low temperature flexibility). Notes on the suitability of each polymer are included.

Table 1. Polymer Properties as a Function of Monomer Selection

Divinylether	Dithiol	Visco-sity (poises)	Hard-ness (Shore A)	% Wt. Gain in JRF Type 1	T_g of Polymer	Notes
DEG-DVE	ECHDT	145	44	27	-53	Wt. gain and T_g too high
DEG-DVE	DMDS	solid	94	3	-63	Solid
DEG-DVE	DMDO	27	25	14	-69	Good candidate
DEG-DVE	HDT	24	25	29	-77	Wt. gain too high
DEG-DVE	DPDM	136	29	45	-46	Wt. gain and T_g too high
Pluriol E-200 DVE	ECHDT	77	43	27	-57	Wt. gain too high; T_g high
Pluriol E-200 DVE	DMDS	41	47	11	-61	OK; prefer lower T_g
Pluriol E-200 DVE	DMDO	59	27	18	-67	Good candidate
BD-DVE	ECHDT	185	42	44	-59	Wt. gain too high
BD-DVE	DMDO	solid	20	21	-79	Solid
HD-DVE	ECHDT	155	50	57	-60	Wt. gain too high
Poly THF DVE	ECHDT	91	30	64	-69	Wt. gain too high
Poly THF DVE	DMDO	27	17	37	-79	Wt. gain too high
TEG-DVE	ECHDT	87	46	26	-55	Wt. gain too high
EG-DVE	ECHDT	193	52	27	-52	Wt. gain, T_g too high
CHVE	ECHDT	4180	51	58	-37	Wt. gain, T_g too high
di-PG-DVE	ECHDT	36	16	20	-61	Good candidate, prefer lower T_g and wt. gain

One of the better candidates is the one containing DEG-DVE and DMDO, so it was selected for further study. This system is essentially linear, so the possibility of solidification at low temperature exists. Materials containing rings, such as ECHDT and CHVE, or pendant alkyl groups, such as the di-PG-DVE, gave liquid products, presumably because the bulky groups would prevent easy solidification. However, some linear systems, such as those containing Pluriol E-200 DVE, also remain liquid even at very low temperatures. A number of systems made with blends of dithiols or divinylethers were also evaluated. Substituting certain amounts of ECHDT or M-DMDS for some of the DMDO prevents solidification at low temperatures even for extended periods.

A polymer containing DEG-DVE, DMDO, and ECHDT also showed promise and was selected for further study. A series of polymers with various molecular weights and functionalities were prepared, based on these monomers. The materials were mixed with 50 phr $CaCO_3$ and cured with a blend of epoxy resins, catalyzed with amine. The tensile and tear strengths, along with the elongation values, are found in Table 2 (next page). Similar studies of polymers with other monomer blends were also completed.

Table 2. Physical Properties of Epoxy-cured Polymers with Various Molecular Weights and Functionalities, Based on DEG-DVE, DMDO, and ECHDT

Molecular Weight	Functionality	Tensile Strength (psi)	Percent Elongation	Tear Strength (pli)
3000	2.05	355	825	60
3000	2.50	260	165	45
3000	2.75	270	95	35
6000	2.05	120	1300+	25
6000	2.50	240	400	60
6000	2.75	195	330	60
4500	2.50	225	210	55
3200	2.20	245	315	70

Based on the information above and from a number of previous experiments, the optimum polymer was determined have a molecular weight of 3200 and a functionality of 2.2. Accordingly, several polymers with this molecular weight and functionality were made with various monomer blends. Using the same criteria outlined above, the three best polymer systems were identified. Physical properties of the polymers and of the polymers cured with the standard epoxy blend are found in Table 3, below.

Table 3. Polymer Characteristics and Physical Properties of Epoxy-cured Polymers Made from Various Monomer Blends

Property	DEG-DVE DMDO	DEG-DVE DMDO ECHDT	DEG-DVE DMDO M-DMDS
Viscosity/poises	63	90	51
T_g polymer/°C	-63	-59	-58
Tensile strength/psi	295	229	252
Percent elongation	390	320	680
Tear strength/pli	73	66	60
% Swell in JRF Type 1 (1 week at 140 °F)	17	21	16
T_g cured system/°C	-59	-50	-53

TASK 2. DEVELOPMENT OF CURING AGENT

In this task, epoxy curing agents were evaluated. The intent was to identify the best type, functionality, and blend of epoxy resins for the curing agent. The ultimate goal was to have a non-chromate containing curing agent, of contrasting color to the base, which could be modified for different worklives of the sealant material. Three curing agents were to be selected.

For the initial screening work, samples of commercially available epoxy resins were obtained. A standard polythioether polymer (DMDO + DEG-DVE) was mixed with 50 phr $CaCO_3$ and cured at 1:1 stoichiometry with the epoxy resins, catalyzed with amine. The specimens were allowed to cure for two days at ambient conditions before being cut and tested. Table 4 contains physical property information on these cured systems.

Table 4. Physical Properties of a Standard Polymer Cured with Various Epoxy Resins

Epoxy	Hard-ness	T_g (°C)	Tensile strength (psi)	% elong -ation	Tear Strength (pli)	% Swell in JRF Type 1
Aromatic epoxies						
Bisphenol A DGE	42	-55	540	900	68	20
Bisphenol F DGE	45	-56	500	900	71	19
Resorcinol DGE	42	-57	325	900	63	18
Bisphenol F novolac	60	-55	250	160	57	17
Aliphatic epoxies						
Butanediol DGE	15	-60	110	1100	24	17
Cyclohexanedimethanol DGE	15	-58	95	1300	18	32
Neopentylglycol DGE	18	-59	150	1300	30	10
Polyglycol DGE	15	-58	125	1275	23	10
Trimethylolpropane TGE	60	-58	240	135	39	18
Cycloaliphatic DGE	NA					
1:1 blend of butanediol DGE and trimethylolpropane TGE	46	-59	257	500	66	19
Other epoxies						
Rubber modified DGE	18	-58	75	1275	20	24
Rubber modified DGE	22	-59	165	1100	31	41
Aromatic tipped aliphatic DGE	30	-57	290	160	47	35

The optimum system would have high tensile and tear strengths, high elongation, low fuel swell, and low T_g for good low temperature flexibility. Some of the epoxy resins in the table were eliminated from further study by their greater swell in fuel, such as the CHDM-DGE, the two rubber modified DGEs, and the aromatic-tipped aliphatic DGE. The remaining aliphatic materials are desirable because of their low T_gs. However, the aromatic materials are desirable because of their good combination of high tensile and tear strengths. Note that the 50:50 blend of BD-DGE and TMP-TGE has a significantly better mix of properties than either material alone, as expected.

Blends of the NPG-DGE and TMP-TGE were then explored. The amount of TMP-TGE was varied from 20 to 70 mole percent. The remainder of the epoxy blend was NPG-DGE, BD-DGE, or a 1:1 mole ratio of the two; this data can be found in Table 5.

Table 5. Physical Properties of a Standard Polymer Cured with Various Blends of Three Epoxies: TMP-TGE, NPG-DGE, and BD-DGE

Epoxy blend								
TMP-TGE	NPG-DGE	BD-DGE	Hardness	T_g (°C)	Tensile strength (psi)	% elongation	Tear Strength (pli)	% Swell in JRF Type 1
20	80	0	35	-58	395	990	58	21
20	40	40	40	-59	245	740	51	19
20	0	80	35	-59	330	920	54	18
30	70	0	44	-59	390	835	66	19
30	35	35	35	-60	420	940	60	18
30	0	70	40	-60	355	900	64	20
40	60	0	45	-59	259	525	70	18
40	30	30	45	-60	370	770	71	20
40	0	60	45	-60	355	710	75	19
50	50	0	50	-59	240	380	64	18
50	25	25	50	-59	250	360	74	18
50	0	50	50	-60	255	300	75	19
60	40	0	55	-59	240	210	62	18
60	20	20	53	-59	235	230	60	18
60	0	40	55	-59	270	200	69	19
70	30	0	55	-59	260	200	56	19
70	15	15	55	-59	255	230	68	19
70	0	30	55	-58	245	200	58	19

As expected, as the trifunctional content increased, the hardness of the cured specimen increased and the elongation decreased. The tensile strength did not increase; instead, it dropped slowly. The tear strength peaked at about 40% TMP-TGE. In most cases, the NPG-DGE and BD-DGE performed comparably; there was no advantage to using a

blend of them. In all cases, swell in JRF Type 1 was similar. The T_gs of the materials were similar and it is expected that they will all have good low temperature flexibility. All systems had relatively low viscosity.

Because tensile strength and elongation are recorded in a number of specifications, the 30% TMP-TGE system was chosen over the 40% system. Based on current cost estimates, NPG-DGE was chosen over BD-DGE. For the initial work, we chose the 30% TMP-TGE, 70% NPG-DGE system for a pure aliphatic epoxy curing agent, noting that an adjustment in functionality might be advisable as we began to formulate. Subsequent work did indicate that a higher functionality material might be preferable.

Recall that the Bis A DGE system had superior tensile and tear strengths but slightly poorer elongation. We therefore explored blends of Bis A DGE with the TMP-TGE/NPG-DGE system to increase the tensile and tear strengths. In this experiment, the mole fraction of TMP-TGE ranged from 30 to 70. For each level of TMP-TGE, the balance was NPG-DGE, Bis A DGE, or a 1:1 (by mole) blend of the two. The data for this experiment is found in Table 6. Two systems had anomalies: the low tensile and tear strengths for the 50:0:50 system and the suspiciously high % elongation for the 60:40:0 system. Since systems not too similar to these were chosen, the cause for the spurious results was attributed to experimental error and not investigated further.

Table 6. Physical Properties of a Standard Polymer Cured with Various Blends of Three Epoxies: TMP-TGE, NPG-DGE, and Bis A DGE

Epoxy blend								
TMP-TGE	NPG-DGE	Bis A DGE	Hard-ness	T_g (°C)	Tensile strength (psi)	% elong-ation	Tear Strength (pli)	% Swell in JRF Type 1
30	70	0	40	-58	415	760	72	18
30	35	35	50	-57	360	600	70	19
30	0	70	55	-56	360	450	93	20
40	60	0	47	-58	295	500	78	20
40	30	30	49	-57	385	660	89	19
40	0	60	55	-56	315	310	101	19
50	50	0	50	-58	260	340	82	19
50	25	25	55	-57	285	300	91	19
50	0	50	60	-56	100	300	24	19
60	40	0	55	-58	290	1010	47	19
60	20	20	55	-57	240	220	80	19
60	0	40	63	-56	320	210	88	18
70	30	0	55	-57	68	210	68	20
70	15	15	57	-57	64	230	64	18
70	0	30	60	-57	65	170	65	18

For the lower levels of TMP-TGE, the elongation dropped as the mole fraction of Bis A DGE increased. Hardness and tear strength increased, but tensile strength did not show marked improvement. At the middle to higher levels of TMP-TGE, the addition of Bis A DGE had less effect on some physical properties. Overall, the swell in JRF Type 1 stayed constant. The T_g differences do not suggest that there would be a significant loss of low temperature flexibility by the use of Bis A DGE over NPG-DGE. However, the viscosity of systems with less Bis A DGE will be lower.

The data from this experiment was entered into a neural network computer program for optimization of TMP-TGE, NPG-DGE, and Bis A DGE levels. The preferred level of TMP-TGE was zero and the amount of NPG-DGE very low. The two best-rated blends suggested by the program were prepared and evaluated. The data from these blends as well as a control of polymer cured with pure Bis A DGE is found in Table 7. The first row of the table contains the data from the initial screening experiment, previously recorded in Table 1.

Table 7. Physical Properties of a Standard Polymer Cured with Blends of Bis A DGE and NPG-DGE

Epoxy blend							
Bis A DGE	NPG-DGE	Hard-ness	T_g (°C)	Tensile strength (psi)	% elong-ation	Tear Strength (pli)	% Swell in JRF Type 1
100	0	42	-55	541	900	68	20
100	0	45	-54	425	1020	80	19
96	4	50	-54	496	990	88	19
93	7	50	-55	560	940	94	21

For two reasons, we choose the 40:30:30 TMP-TGE:NPG-DGE:Bis A DGE system over those suggested by the neural network. First, the viscosity of the blend containing less Bis A DGE will be significantly lower; this had not been entered as a parameter. Second, the T_g of that system is lower, indicating better low temperature flexibility.

Previous work within PRC-DeSoto International has shown that a 60:40 (by weight) mix of Bis A DGE and a Bis F novolac gives good properties. Because of our experience with this standard system, we offer it as a curing agent choice, even though the viscosity is higher than the aliphatic-containing systems. The T_g is also slightly higher.

To summarize, the three curing agents we have selected are the following:

1. 30: 70 (by mole) blend of TMP-TGE and NPG-DGE
2. 40:30:30 (by mole) TMP-TGE: NPG-DGE, and Bis A DGE
3. 60:40 (by weight) blend of Bis A DGE and Bis F novolac

For ease of reference, the physical properties for these three systems are collected below in Table 8.

Table 8. Physical Properties of a Standard Polymer Cured with the Three Selected Epoxy Curing Agents

Epoxy System	Hard-ness	T_g (°C)	Tensile strength (psi)	% elong-ation	Tear Strength (pli)	% Swell in JRF Type 1
30:70 TMP-TGE, NPG-DGE	44	-59	390	835	66	19
40:30:30 TMP-TGE, NPG-DGE, and Bis A DGE	49	-57	385	660	89	19
60:40 (by wt.) Bis A DGE, Bis F novolac	50	-55	331	450	90	18

TASK 3. DEVELOPMENT OF A CORROSION-INHIBITING AGENT

The replacement of chromates as corrosion-inhibiting agents for aircraft aluminum is a difficult task. One reason is that chromate performs a number of different functions, including the ability to be adsorbed onto a bare metal or metal oxide surface after it exits the carrier matrix. In PRC-DeSoto International's search for equivalent non-chromate inhibitors, a number of chromate functions were identified; no single material has yet been found to fulfill all of these functions.

PRC-DeSoto International has identified a number of packages of multi-component inhibitors to replace chromate (US Patent 5,951,747, Lewis and Aklian). These corrosion inhibitor packages consist of synergistic combinations of inhibitors designated by letters which denote a subgroup of compounds. The packages can be defined as follows: at least one from the group consisting of phosphates, phosphosilicates, silicates, and mixtures thereof (e.g., C, H); at least one from the group consisting of titanates, zinc salts, and mixtures thereof (e.g., N, Z, W); and preferably also containing a borate and a succinate (e.g., B, I). From solution electrical impedance spectroscopy results, the following packages are ordered by effectiveness: BCINZ; HINZ; HIN; IN; IW; I; W; BCNZ; HNZ; HN.

The choice of inhibitor package is dependent upon a number of factors, such as the cure chemistry of the sealant, the intended substrate(s), and the range of exposure conditions for the final product. Further, the effect of inhibitors on the final properties of the sealant cannot be discounted. The goal for this task was to assess inhibitor candidates by electrochemical activity, reactivity, and compatibility with the polymer and curing agents selected, as well as the ability to inhibit corrosion on a wide variety of substrates. Three packages were to be chosen for subsequent sealant development.

The first concern was to ensure that the inhibitors themselves would not compromise storage stability. Interference of an inhibitor with either the polythioether or the epoxy could be overcome by placing that material with the other component. Materials that interfere with both will not be used.

To check for interference, 5% by weight of a number of inhibitors from the different subgroups were mixed with several polymers and several epoxies. Two polymers chosen were the P-3.1 based on DEG-DVE/DMDO and its hydroxyl-terminated counterpart. The hydroxyl-terminated material was included in the evaluation in case all mercaptan-terminated materials failed. Two other polythioethers, P-3.1b and Permapol P-3.2 (US Patent 5,959,071; DeMoss and Zook), were included. For epoxies, Bis A DGE, Bis F DGE, a Bis F novolac, and a waterborne epoxy were selected. The inhibitors chosen were two versions of B (designated B1 and B2), C, H, I, N, W, and Z. The mixtures were then placed in the 120 °F oven and checked periodically.

Appearance and viscosity were monitored for several months. Simplified results are found in Table 9 (next page), in which "OK" indicates minimal, if any, change in appearance or viscosity after at least two months at 120 °F. "X" indicates that there

was an unfavorable interaction. However, some of these interactions were much more significant than others. For instance, B1 cured the epoxies solid in less than one week; C gave only a small viscosity change in two of the four epoxies after one month.

Table 9. Stability of Inhibitor Components Mixed with Polymers or Epoxies

Polymer	B1	B2	C	H	I	N	W	Z
P-3.1b	X	X	OK	X	OK	X	OK	OK
P-3.1 standard	X	X	OK	X	OK	X	X	OK
P-3.2	X	X	OK	X	OK	OK	X	X
OH term P-3.1	X	X	OK	X	OK	OK	X	OK
Bis A DGE	X	OK	OK	OK	X	OK	OK	OK
Bis F DGE	X	OK	OK	OK	X	OK	OK	OK
Bis F novolac	X	OK	X	OK	X	OK	OK	OK
W/B epoxy	X	OK	X	OK	X	OK	X	OK

The results can be summarized as follows:

1. C and I were more compatible with the polymers and should preferably be placed in the base. However, C had less interaction with epoxies than I and could possibly be placed in the epoxy.

2. B2 had significant interactions with some polymers and should be placed in the epoxy only. H, N, and W were more compatible with the epoxy than the polymers, but the polymer interactions were not generally serious.

3. Z was compatible with both polymer and epoxy and can be placed in either side.

4. B1 is not compatible with either polymer or epoxy and cannot be used. Therefore, the designation B means only B2 from this point on.

The next step was to determine the effect of the inhibitors on sealant properties, such as cure rate, hardness, tensile and tear strengths, percent elongation, and swell in fuel. Individual inhibitors and several packages were used in a simple formula described in Task 4 (next section); the inhibitors are substituted for an equivalent weight of alumina. The polymer used was the one based on DEG-DVE and DMDO; the curing agent contained the 60:40 blend of Bis A DGE and Bis F novolac.

Two levels (5 and 20 phr) of the individual inhibitors B, C, H, I, N, W, and Z were used. Several packages were also investigated: BCINZ, BCNZ, HNZ, and HN. Two inhibitor levels were used: one with 5 phr of each inhibitor and another with a total of 20 phr with the inhibitors used at equal weight ratios. Two controls were also included: one with no inhibitors at all (therefore containing the full 20 phr of alumina) and the other containing 10 phr each of strontium and calcium chromates. The first experiments were done with

1 phr of the tertiary amine catalyst; because many cures were slow, the experiment was repeated with 2.5 phr catalyst. The results from this experiment are found in Table 10.

Table 10. Physical Properties of a Standard Sealant Containing Various Levels of Different Non-chromate Corrosion Inhibitors

Inhibitor						JRF Type 1		Salt Water	
Type	Level (phr)	Hard-ness	Tensile strength (psi)	% Elonga-tion	Tear strength (pli)	% swell	% wt. loss	% wt. gain	% wt. loss
None	0	60	210	165	41	17	1.9	2.5	1.8
Cr	20	60	235	150	64	16	1.7	8.7	2.6
B	5		Samples containing B cured too slowly to be tested						
B	20								
C	5	64	335	180	65	12	2.8	2.1	2.9
C	20	63	310	175	64	11	4.4	2.6	5.3
H	5	63	320	180	61	15	1.9	1.3	3.5
H	20	62	305	175	75	17	1.9	1.8	1.4
I	5		Samples containing I cured too slowly to be tested						
I	20								
N	5	60	310	190	65	16	1.1	6.7	2.3
N	20	60	240	180	64	19	2.0	16.4	1.9
W	5	60	300	250	69	16	1.7	4.6	1.7
W	20	50	255	410	59	16	1.4	8.3	2.7
Z	5	60	260	160	37	15	2.1	2.2	1.7
Z	20	57	245	140	63	15	1.9	2.7	2.0
BCINZ	20		Samples containing B or I cured too slowly to be tested						
BCNZ	20								
HNZ	15	60	350	190	97	15	2.0	4.8	2.0
HNZ	20	60	240	210	35	18	1.7	5.1	2.2
HN	10	45	193	180	40	18	1.9	4.9	2.1
HN	20	48	185	220	42	16	1.4	7.9	1.3

Sealants containing B or I cured too slowly to be tested, even at the higher level of catalyst. Although samples containing C or W had slower cure rates, they did achieve full cure. Because two of the inhibitor packages used contained B and I, they did not cure properly. Several additional packages were included in the next round of testing.

Most of the sealants with inhibitors had hardness, tensile and tear strengths, and elongation values equal to or better than the control with no inhibitor. Fuel resistance was not compromised by the presence of the inhibitors; only sealants with C showed significantly greater weight loss after drying than the controls. However, there was a much larger variation in weight gain in salt water. Some samples, such as those with just C, H, or Z had little weight gain when kept in jars of 3% salt water for one week at 140 °F; others took up considerably more, such as those containing N or W. Although

the sealant with the higher level of C did have a higher weight loss after drying, the other materials showed little difference compared to the control.

The effectiveness of the corrosion inhibitors in an actual sealant was determined using both EIS (electrochemical impedance spectroscopy) and I_{galv} (galvanic current) measurements. A detailed description of these methods can be found in an article entitled "Quantitative Methods of Predicting Relative Effectiveness of Corrosion-Inhibiting Coatings on Aircraft Aluminum" by Lewis, et. al in the ACS Symposium Series book Organic Coatings for Corrosion Control (edited by Gordon P. Bierwagen). A updated version entitled "Development of Chromate-free Inhibitors for Aircraft Aluminum Alloys" by K. Lewis can be found in the Proceedings of the 5th International Aerospace Corrosion Control Symposium, Amsterdam, the Netherlands, Nov. 99. Brief descriptions of the two methods follow.

Electrical impedance spectroscopy, EIS: A disk is cut from a thin film of sealant, about 10 - 15 mils thick, and placed onto a plastic screen atop the substrate. In this case, the substrates used are Scotchbrite-abraded 2024 and 7075, aluminum alloys commonly used on aircraft. The plastic screen serves to keep the sealant from becoming bonded to the substrate. An acrylic cylinder is placed on top of the sealant; an O-ring is used to ensure that the system is watertight. The cylinder is filled with an aqueous salt solution. A passivated stainless steel counter-electrode and calomel reference electrode are placed in the solution and held with a rubber stopper about one inch above the sealant sample atop the working aluminum electrode. A potentiostat with a frequency response analyzer is used to make the measurements.

After soaking overnight, a resistance value, R_{pore}, is measured; R_{pore} is a measure of the barrier properties of the sealant. The higher the value, the better; since these sealants are not particularly sensitive to water, the values are expected to be high. The sealant is then slit in five places with a razor blade and the salt solution forced underneath the sealant; a syringe is used to push out any air bubbles. Measurements are begun at about four hours and continue as the salt solution leaches inhibitor from the sealant, especially in the confined space under the sealant, simulating anaerobic blister or crevice conditions. The charge transfer resistance, R_{ct}, measured on the known metal area determines the electrochemical activity of the inhibitor in the film. Again, higher values indicate better performance. This value, R_{ct}, is measured at various intervals (four hours, one day, one week, two weeks, and so on) to determine if protection against corrosion is maintained. Samples are monitored until a good comparison of all packages can be made; this usually requires a minimum of one month.

Galvanic current (I_{galv}) measurements: In the galvanic current test cell configuration, the development of acidic crevice conditions is accelerated. In this system, the titanium counter-electrode and the metal substrate are shorted electrically. The metal substrates, again Scotchbrite-abraded 2024 and 7075, are first coated with a thin layer of sealant; a bare area is left to produce the galvanic signal. An aqueous salt solution is again used and the inhibitors are leached from the film to passivate the bare area.

Since the gap between the two metals is small, the oxygen is depleted and a crevice environment is created. This process takes between 100 and 1000 hours.

After four to nine weeks, the samples used for the EIS testing were disassembled and the condition of the two substrates noted. The I_{galv} samples were evaluated after 300 hours of current flow. The appearance of each substrate is graded based on a scale of 0 to 25, as outlined in Table 11. A wide scale was used since some effects are considered more serious than others and we wished to be able to differentiate the materials easily with a final numerical value. In our visual rankings, we viewed pitting as a more destructive form of corrosion than overall discoloration or uniform corrosion. Localized corrosion will more greatly diminish the structural integrity of an aircraft part by generating stress risers which initiate cracks. Note also that the I_{galv} grades are usually higher than the EIS grades; the test is considered harsher.

Table 11. Scale for Ranking EIS and I_{galv} Samples

Grade	Description; explanation
0	Surface is bright and shiny; no pits or discoloration
1 - 2	A few yellow specks, visible only under a microscope, may indicate the start of a pit
3 - 4	The very few incipient black pits are more defined, but a microscope is still required to see them
5 - 7	Very small pits and/or discoloration more noticeable; these can be seen with the naked eye
8 - 10	A few obvious pits and faint discoloration
11 - 14	Obvious corrosion product on pits and some overall white haze, indicating uniform (as opposed to localized) corrosion
15 - 20	Quite a few obvious pits and/or phase area corrosion (on 7075); also, significant white haze from uniform corrosion
21 - 25	Gross pitting, large amount of white corrosion product

Pictures of panels used for the EIS and I_{galv} experiments for a number of the inhibitor packages can be found in Appendix 2. Graphs of the EIS data (log R_{ct} vs. time) were also plotted; some are included in Appendix 3. Please note that the lines in the figures in Appendix 3 are drawn solely to guide the eye. The interpretation of such graphs is not simple since the appearance of the substrate at the end of the run is dependent upon several factors. First, the inhibitor must leach out rapidly enough to form a passivation layer relatively quickly: if the leach rate is too slow, corrosion will have a chance to begin. Second, some passivation layers are more effective than others in preventing corrosion.

In general, if resistance is high early in the experiment and remains high, the substrate will have a good appearance. However, defects may occur because of corrosion or because an air bubble has somehow become trapped between the substrate and the sealant sample. In these cases, the resistance value may not correlate as well with the

appearance of the substrate. In all cases reported here, both EIS curves and appearance of the substrate were used to rank the effectiveness of the inhibitor.

As with the EIS data, it is ideal to use the graph of the galvanic current measurement vs. time to rank the substrates. Unfortunately, the equipment used to measure the galvanic current failed early in the experiment; the graphs were therefore not as useful as those reported in the referenced literature. Although the equipment was partially repaired and measurements taken, the useable data set is incomplete. Therefore, only visual assessment was used to rank the I_{galv} samples. Attempts to salvage the more quantitative numerical data were not successful. However, failure of the current measuring device does not alter the results of the exposures. Table 12 compares the rankings of various inhibitor packages, based on both EIS and I_{galv} exposures. The table also contains columns with the sum of the rankings for both methods for each substrate as well as the total sum of all four tests for each inhibitor.

Table 12. Rankings of Various Inhibitors on Both 2024 and 7075, Using Both EIS and Galvanic Current Measurements

Inhibitor package	EIS 2024	Igalv 2024	EIS 7075	Igalv 7075	sum 2024	sum 7075	total sum
none	25	25	21	24	50	45	95
Cr at 20 phr	1	3	2	14	4	16	20
C at 5 phr	13	24	17	16	37	33	70
H at 5 phr	25	21	25	20	46	45	91
N at 5 phr	11	13	13	25	24	38	62
W at 5 phr	10	7	5	16	17	21	38
Z at 5 phr	16	12	9	22	28	31	59
C at 20 phr	8	10	17	12	18	29	47
H at 20 phr	23	24	12	18	47	30	77
N at 20 phr	9	12	8	24	21	32	53
W at 20 phr	4	11	0	10	15	10	25
Z at 20 phr	23	20	10	14	43	24	67
CW at 10 phr each	0	10	2	12	10	14	24
HN at 5 phr each	24	23	11	21	47	32	79
HN at 10 phr each	11	15	9	21	26	30	56
HW at 10 phr each	6	21	6	18	27	24	51
CHW, 20 phr total	2	9	1	15	11	16	27
CNW, 20 phr total	0	10	4	8	10	12	22
CNZ, 20 phr total	5	15	4	15	20	19	39
HNW, 20 phr total	7	22	12	14	29	26	55
HNZ, 15 phr total	24	22	13	25	46	38	84
HNZ, 20 phr total	12	15	13	22	27	35	62
CHNW, 20 phr total	4	9	2	12	13	14	27

Not unexpectedly, the chromate-containing sample had the best (lowest) total sum; the uninhibited, the worst. Figures 1 and 2 contain photographs of these substrates after testing. The substrates for the chromate-containing sealant look virtually untouched, except for the I_{galv} 7075 substrate, which did show signs of corrosion. Although Figure 2 does show that the substrates for uninhibited materials look significantly worse, the pitting and amount of corrosion product is actually even greater than the photographs indicate. The EIS curves for both chromate and uninhibited materials are found on each of the graphs in Appendix 3 for ease of comparison.

In general, increasing the inhibitor level increased its effectiveness in preventing corrosion in both EIS and I_{galv} testing. Figure 3 contains photographs of substrates from sealants with 5 phr of inhibitor C; Figure 4 is from those containing 20 phr. These photographs also clearly show phase area corrosion on 7075. Also, compare the rankings of inhibitors other than Z at 5 and 20 phr, or the HN or HNZ packages at their two different levels. Z is a noticeable exception to this rule; note also the shape of the EIS curve on 7075 in Figure 12. At about two weeks, the curve peaks and then drops. For this material, an insoluble hydroxide layer will form initially on alkaline cathode sites but will begin to re-dissolve as oxygen depletes and the pH starts to drop.

Some materials performed better on one substrate than the other; an ideal inhibitor would perform well on both substrates under both test conditions. Figures 11 and 12, which contain the EIS curves for the single inhibitors at 20 phr, are instructive. Note that in Figure 11, all sealants containing inhibitors had higher resistance values than the uninhibited sealant after two weeks on 2024; this was not true for 7075 (Figure 12). However, the actual appearance of the substrates was better for the sealants containing inhibitors than for the one that did not. C and W both had initial values that were higher than that of chromate on 2024, but the appearance of the substrate is not as good. Although W always had a higher resistance than chromate on 2024, the substrate did look poorer. Nevertheless, EIS curves certainly do indicate something about performance. On 2024, the resistance values of H and Z alone are similar to that of the uninhibited material, and indeed, the same is true of the appearance of the substrate. On 2024, N and C gave lower values than chromate, but higher than those of H and Z; the appearance of the substrates correlates with this.

The synergistic effects of inhibitors can be seen in the EIS curves in Figures 13 and 14. Note that on 2024 (Figure 13), the initial and final values of the CNZ package were, in general, noticeably higher than those for the single inhibitors. Note that C alone had a high initial value on 2024; this was true for many C-containing packages. On 7075 (Figure 14), C, N, and Z had final values lower than that of the uninhibited material. However, the CNZ package values were higher. Although the appearance of the 7075 substrate with the CNZ sealant was not better than that of chromate, it was quite good and certainly better than that of any of the three inhibitors alone. Photographs of the substrates with 20 phr C, N, and Z are found in Figures 4, 5, and 6; Figure 7 contains photographs of the CNZ package at a total inhibitor level of 20 phr.

Additional factors other than EIS and I_{galv} rankings need to be considered when selecting the final packages. Recall that both C and W caused the sealants to cure more slowly. Sealants containing the individual inhibitors N and W gained more weight in salt water, but the inhibitors apparently did not leach out to a large extent. C did leach out in both salt water and fuel. In order to be effective, the inhibitors must be able to leach out from the sealant to protect the metal, but too high a leach rate could be unfavorable in the long term. Neither the EIS nor I_{galv} tests, as run, measure depletion effects. These tests can be modified to do so; also, cyclic salt fog or alternate immersion/emersion testing could be used.

Mixtures of inhibitors are expected to perform better than individual components at the same total inhibitor level, as in noted for CNZ (total sum is 39, significantly lower than the values for C, N, or Z individually). A notable exception is W, which has a good ranking at 20 phr when used by itself. However, its total ranking is influenced by its superior performance on 7075; C-containing materials were often better on 2024.

For the final selection of packages, we looked at the following: performance on both substrates in both corrosion tests, effect on cure and sealant properties, and leach rates of inhibitors in both water and fuel. Using these criteria, we selected the following packages: CNW, CHW, and CHNW. Photographs of substrates for these packages can be found in Figures 8, 9, and 10; graphs containing the EIS curves of the selected packages on both 2024 and 7075 can be found in Figures 15 and 16.

TASK 4. DEVELOPMENT OF PROTOTYPE SEALANT FORMULATION

A prototype sealant formula, with weights to the nearest 1 phr, can be found in Table 13. This formula is based on previous work performed by PRC-DeSoto International.

Table 13. Prototype Sealant Formulation (No Inhibitors)

Base		Accelerator	
Material	**Level**	**Material**	**Level**
Polymer	100	Epoxy	100
Calcium carbonate	55	Calcium carbonate	60
Alumina	20	Silane	10
Plasticizer	5	Carbon black	10
Solvent	5		
Magnesium oxide	1		
Phenolic resin	1		
Tertiary amine	1		

Table 14 contains the physical properties of the nine combinations of three sealant bases and three epoxy curing agents in a prototype formula. No inhibitors are included at this stage.

Table 14. Physical Properties of the Nine Combinations of Three Sealant Bases and Three Epoxy Curing Agents in a Prototype Formula with No Inhibitors

Polymer System 1 (PS1) DEG-DVE + DMDO
Polymer System 2 (PS2) DEG-DVE + DMDO + ECHDT
Polymer System 3 (PS3) DEG-DVE + DMDO + M-DMDS

Epoxy System 1 (ES1) 30:70 (by mole) TMP-TGE:NPG-DGE
Epoxy System 2 (ES2) 40:30:30 (by mole) TMP-TGE:NPG-DGE:Bis A DGE
Epoxy System 3 (ES3) 60:40 (by weight) Bis A DGE:Bis F novolac

Polymer/Epoxy System	Hardness (Shore A)	Tensile Strength (psi)	Percent Elongation	Tear Strength (pli)	% Swell in JRF Type I
PS1 + ES1	55	450	850	85	14.5
PS1 + ES2	55	400	650	90	12.4
PS1 + ES3	60	350	600	90	12.7
PS2 + ES1	50	350	825	58	19.5
PS2 + ES2	58	275	425	85	16.9
PS2 + ES3	62	325	400	80	16.2
PS3 + ES1	45	300	800	50	13.7
PS3 + ES2	55	275	350	75	12.4
PS3 + ES3	55	300	450	75	12.3

In several cases, the 30:70 TMP-TGE:NPG-DVE epoxy system gave significantly softer cures than the other epoxy systems. To compensate for this, we can increase the functionality of the system by using a 40:60 blend, as noted in Task 2; this will be done if this curing agent is desired for further work.

Samples of the polymers, epoxy blends, and prototype bases and accelerators without inhibitors were prepared for shipment to other team members. The samples shipped from the Burbank research laboratories on July 14, 2000.

Incorporation of the inhibitor packages necessitates modification of the formula. Recall that only component C could safely be put into the base. The other two or three inhibitors in the selected packages, (W and H or N), should go into the accelerator. Since the interaction of C with the epoxy was low, it was decided to put it into the accelerator as well, thus obviating the need to make more than one base for all three packages.

In order to keep the level of inhibitor the same as that used for the foregoing experiments, a large quantity of dry material must be added to the accelerator side, making processing difficult. Accordingly, some of the plasticizer was removed from the base and placed into the accelerator; the calcium carbonate was removed from the accelerator and placed into the base. To keep the VOC as low as possible, the solvent was removed from the base. To ensure that the material would cure fully, a high level of catalyst is used.

The modified formula is found in Table 15. Note that the quantities of the inhibitors depend upon which package is being employed. In the accelerator formulation, 45 phr of each of the four inhibitors corresponds to 5 phr each (20 phr total) if the inhibitors had been placed in the base; 60 phr of three inhibitors corresponds to about 6.6 phr each, also for a total of 20 phr.

Table 15. Prototype Sealant Formulation with Corrosion Inhibitors

Base		Accelerator	
Material	**Level**	**Material**	**Level**
Polymer	100	Epoxy	100
Calcium carbonate	61	Silane	12
Plasticizer	3	Carbon black	8
Magnesium oxide	1	Plasticizer	22
Phenolic resin	1	Inhibitor C	45 or 60
Tertiary amine	3.5	Inhibitor H	45 or 60
		Inhibitor N	45 or 60
		Inhibitor W	45 or 60

The formula in Table 15 was used with the DEG-DVE/DMDO polymer and the Bis A DGE/Bis F novolac epoxy blend. The physical properties of this system with the three inhibitor packages is found in Table 16.

Table 16. Physical Properties of Systems Containing Corrosion Inhibitors

Property	Base	CHNW	CNW	CHW
Specific gravity	1.37	1.66	1.60	1.67
Viscosity/poises	10,800	2,100	2,280	2,720

BASE + ACCELERATOR	CHNW	CNW	CHW
Flow/inches	< 0.1	< 0.1	< 0.1
Application time/minutes	30	30	30
Tack-free time/hour	4	4	4
Standard cure time/hours	24	24	24
Hardness/Shore A	63	60	63
Tensile strength/psi	305	280	350
% elongation	310	435	390
Tear strength/pli	75	73	80

Samples of each of these three systems will be shipped to UDRI by August 31, 2000.

SUMMARY

From extensive screening work, three polymers with optimized molecular weight (3200) and functionality (2.2) were identified. These polymers are identified as follows:

1. DEG-DVE + DMDO
2. DEG-DVE + DMDO + ECHDT
3. DEG-DVE + DMDO + M-DMDS

A large number of single epoxy resins and blends were evaluated. From this work, three epoxy resin blends were selected. They were identified as follows:

1. 30: 70 (by mole) blend of TMP-TGE and NPG-DGE (Subsequent work with the formulated sealant indicated that a 40:60 ratio would be preferable.)
2. 40:30:30 (by mole) TMP-TGE: NPG-DGE, and Bis A DGE
3. 60:40 (by weight) blend of Bis A DGE and Bis F novolac

Non-chromate, corrosion inhibitors were identified by PRC-DeSoto International in earlier work. A number of likely candidates were assessed for stability with several polymers and curing agents. Based on this information, some were eliminated from further investigation. This experiment also determined placement of the inhibitors, that is, whether they can be placed in the base or in the accelerator of the two-part system. The effects of single inhibitors and a number of inhibitor packages on the physical properties of a prototype sealant were determined. Because of extremely slow cure rates, even at high levels of catalyst, some inhibitors were eliminated from further study.

Two different methods were used to determine the effectiveness of the candidate corrosion inhibitor packages on both 2024 and 7075 aluminum alloys. The methods chosen were electrical impedance spectroscopy (EIS) and galvanic current (I_{galv}) measurements. Both visual examination of the substrates and numerical data generated during the test were used to rank the EIS samples; only visual inspection was used for the I_{galv} samples. Based on the effectiveness of corrosion inhibition under these conditions and the effects of the inhibitors on the physical properties of the sealants, three inhibitor packages were chosen: CNW, CHW, and CHNW.

A prototype sealant formulation (without inhibitors) was identified. Physical properties of all combinations of the selected polymers and epoxies were obtained; by doing so, it was determined that one curing agent system required an increase in functionality, as noted above. After the inhibitor packages were selected, the prototype sealant formulation was adjusted to accommodate the inhibitors.

Polymers and curing agents were submitted to other team members for evaluation. Bases and accelerators based on the prototype sealant formulation, without inhibitors, were also distributed. As per the contract, samples of bases and accelerators containing the non-chromate corrosion inhibitor packages will be delivered if desired.

Figure 1: 20 phr Chromate in Sealant:
Substrates after EIS and Igalv Testing

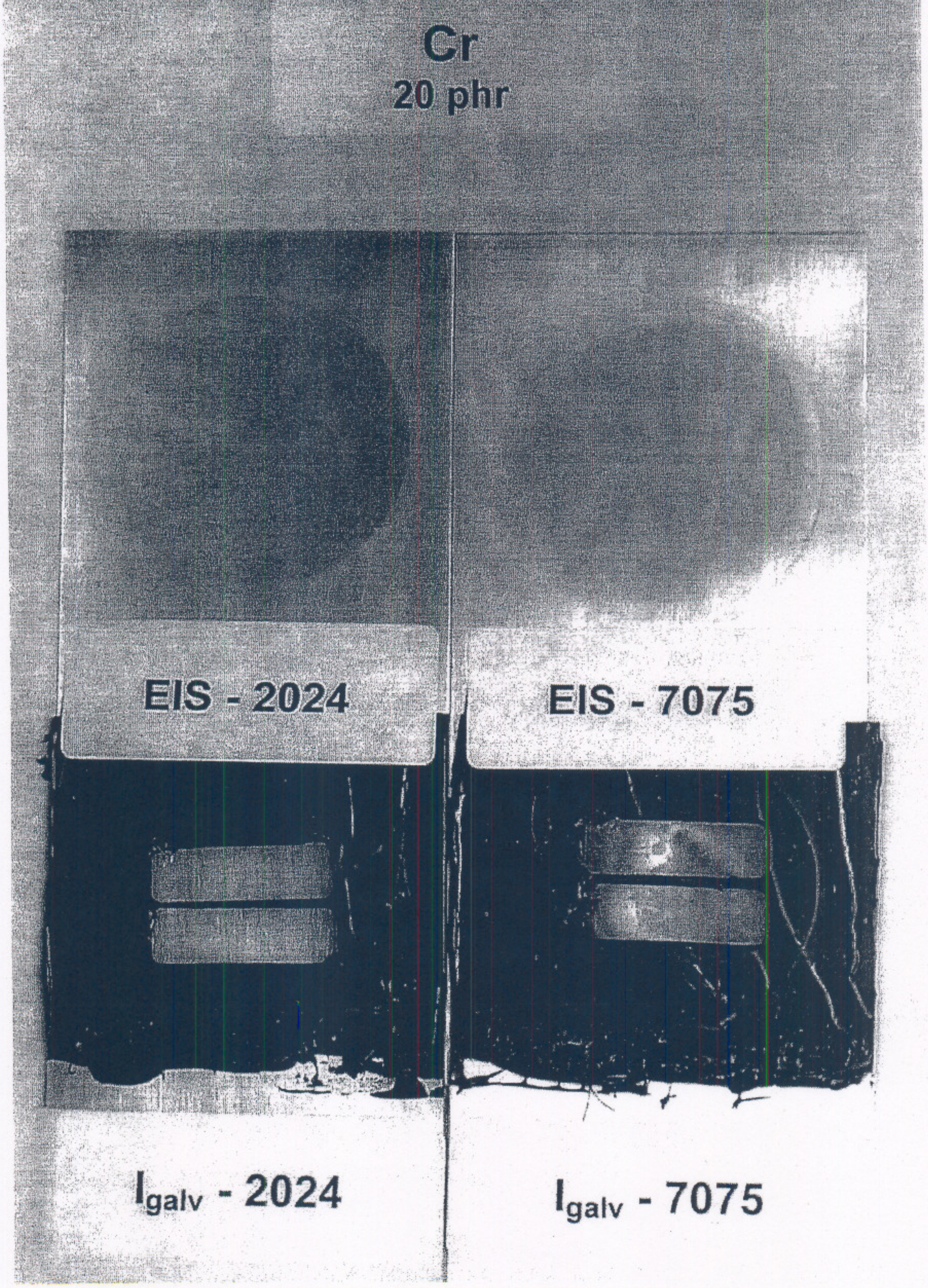


Figure 2: No Inhibitors in Sealant:
Substrates after EIS and Igalv Testing

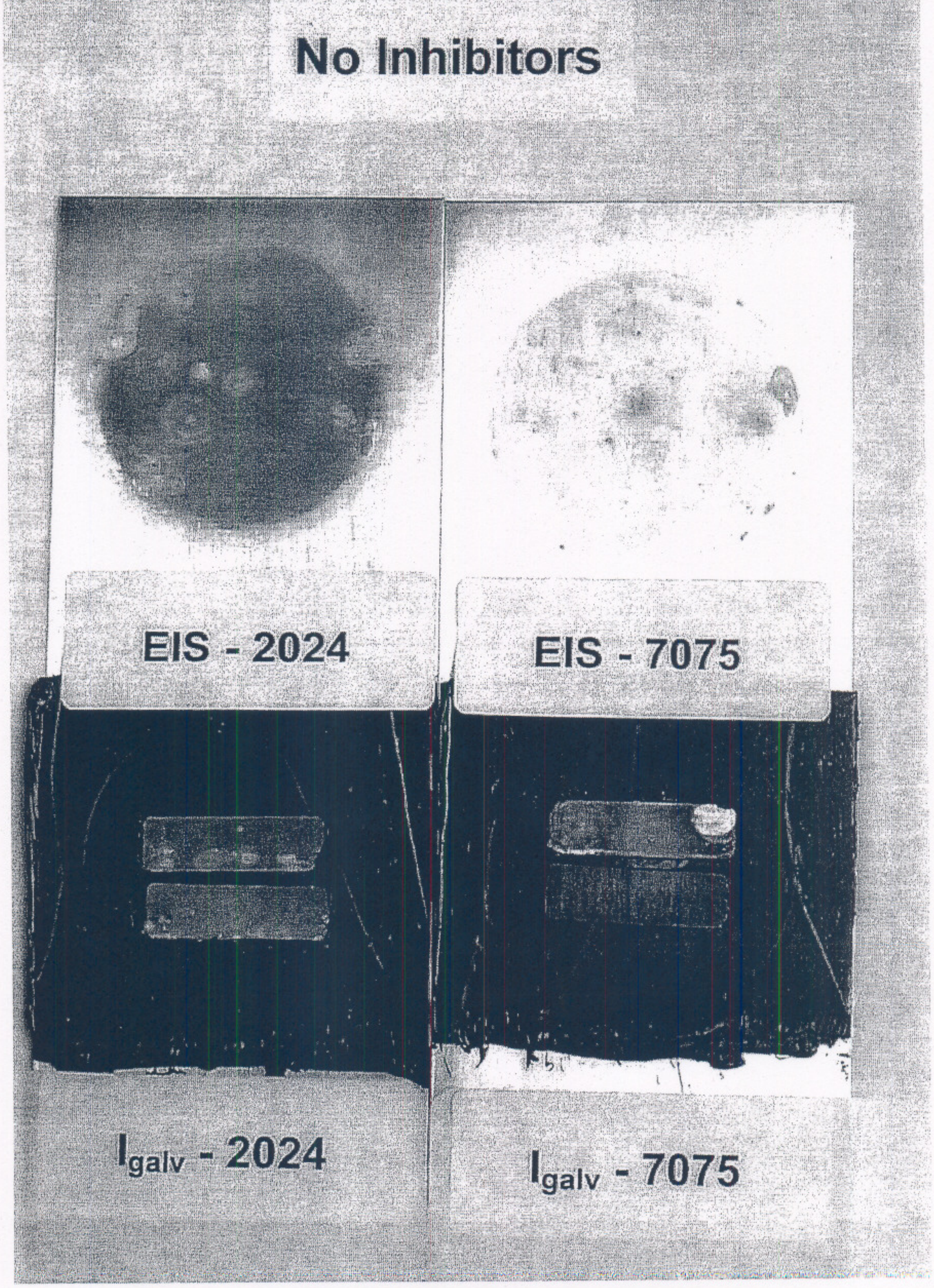


Figure 3: 5 phr C in Sealant:
Substrates after EIS and Igalv Testing

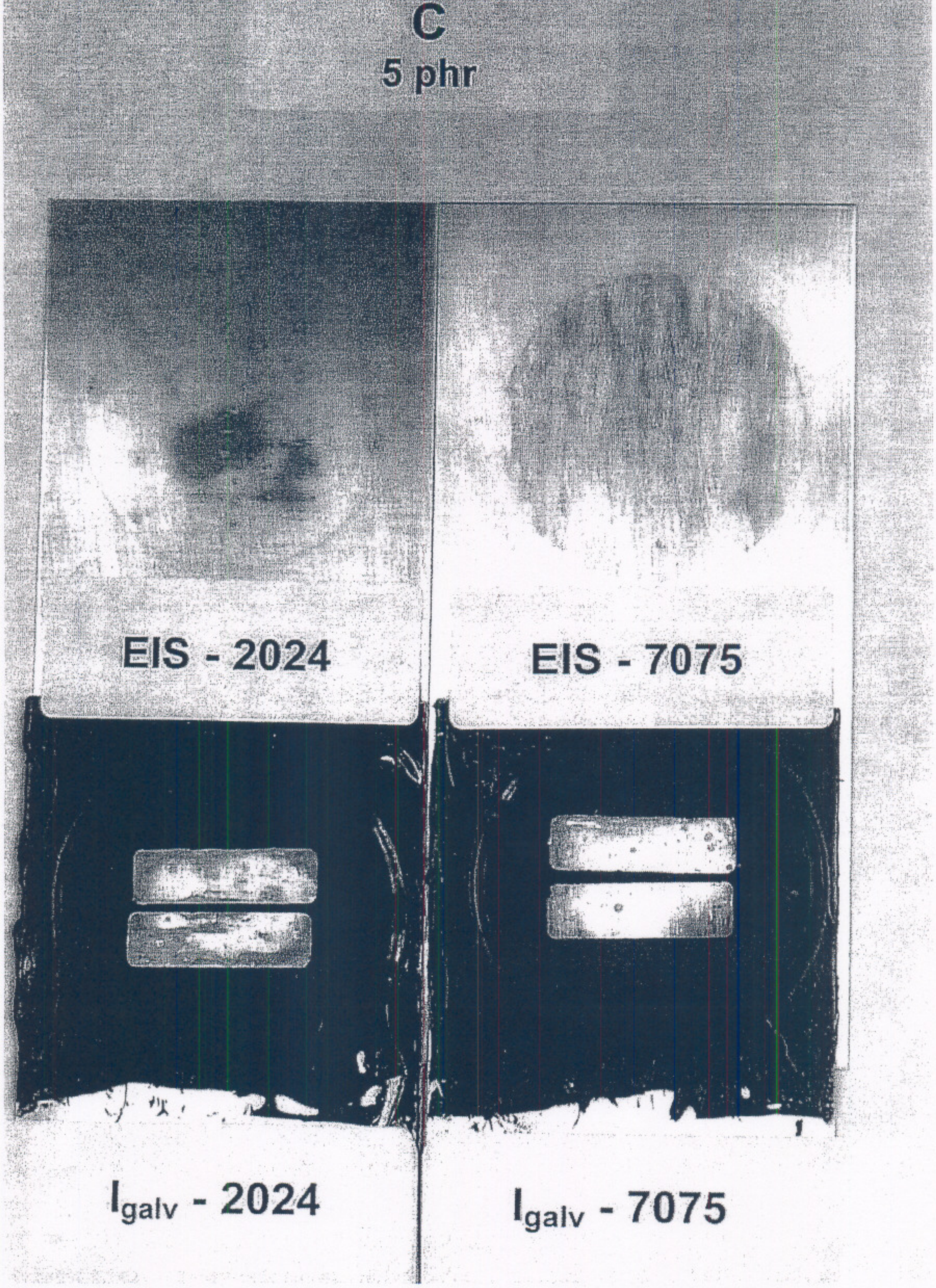


Figure 4: 20 phr C in Sealant:
Substrates after EIS and Igalv Testing

Figure 5: 20 phr N in Sealant:
Substrates after EIS and Igalv Testing

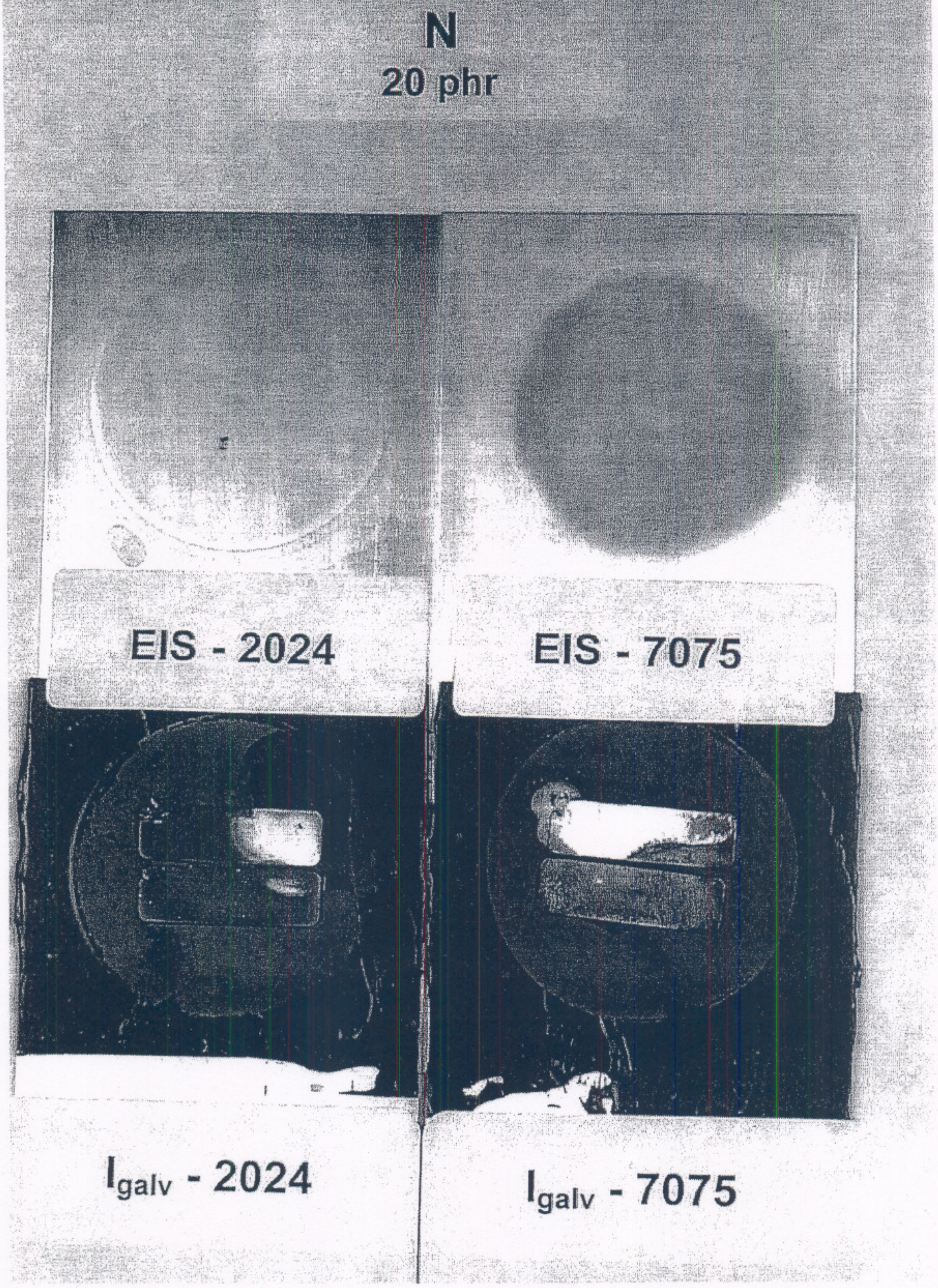


Figure 6: 20 phr Z in Sealant:
Substrates after EIS and Igalv Testing

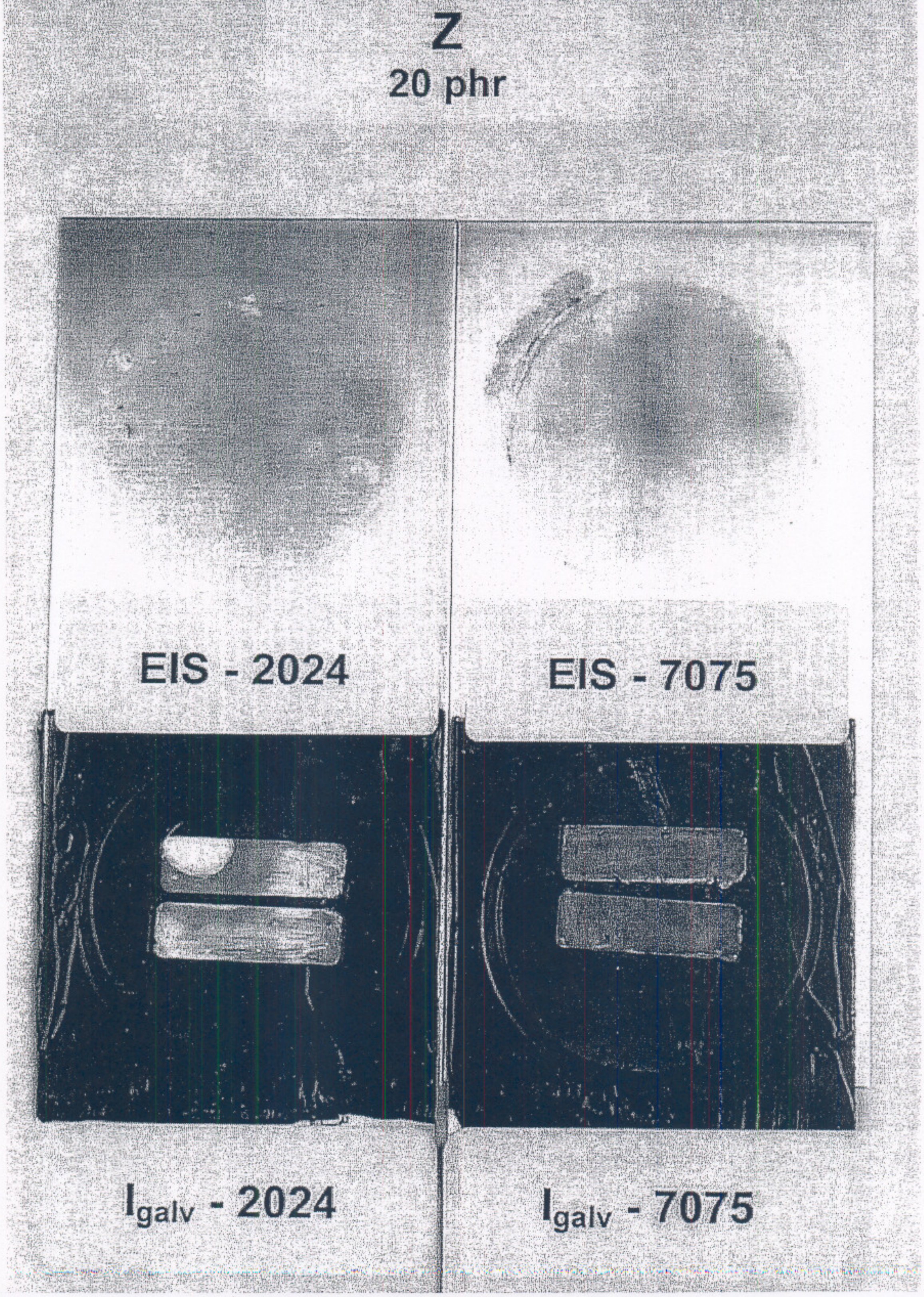


Figure 7: 6.6 phr Each of C, N, and Z in Sealant: Substrates after EIS and Igalv Testing

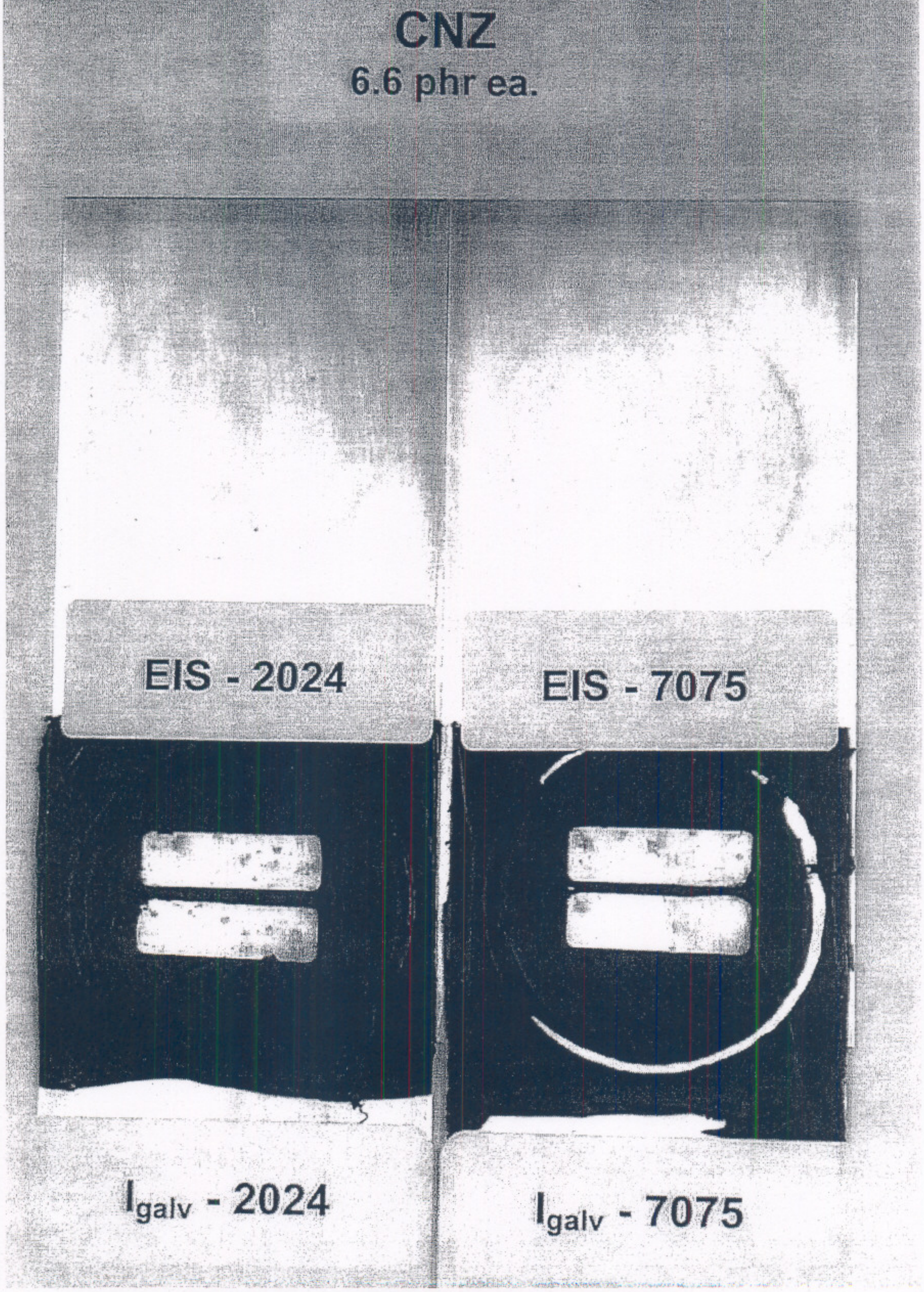


Figure 8: 6.6 phr Each of C, N, and W in Sealant:
Substrates after EIS and Igalv Testing

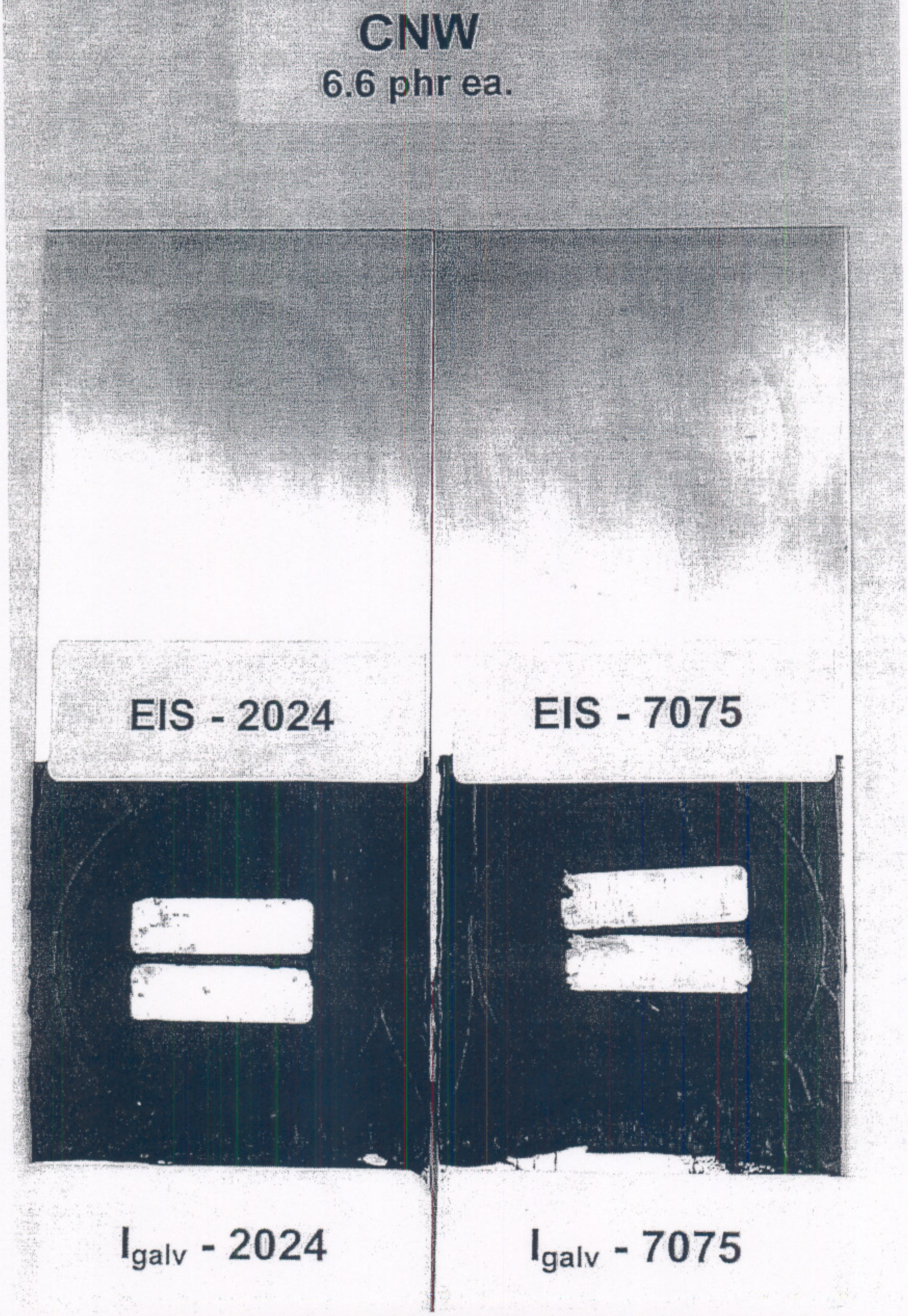


Figure 9: 6.6 phr Each of C, H, and W in Sealant: Substrates after EIS and Igalv Testing

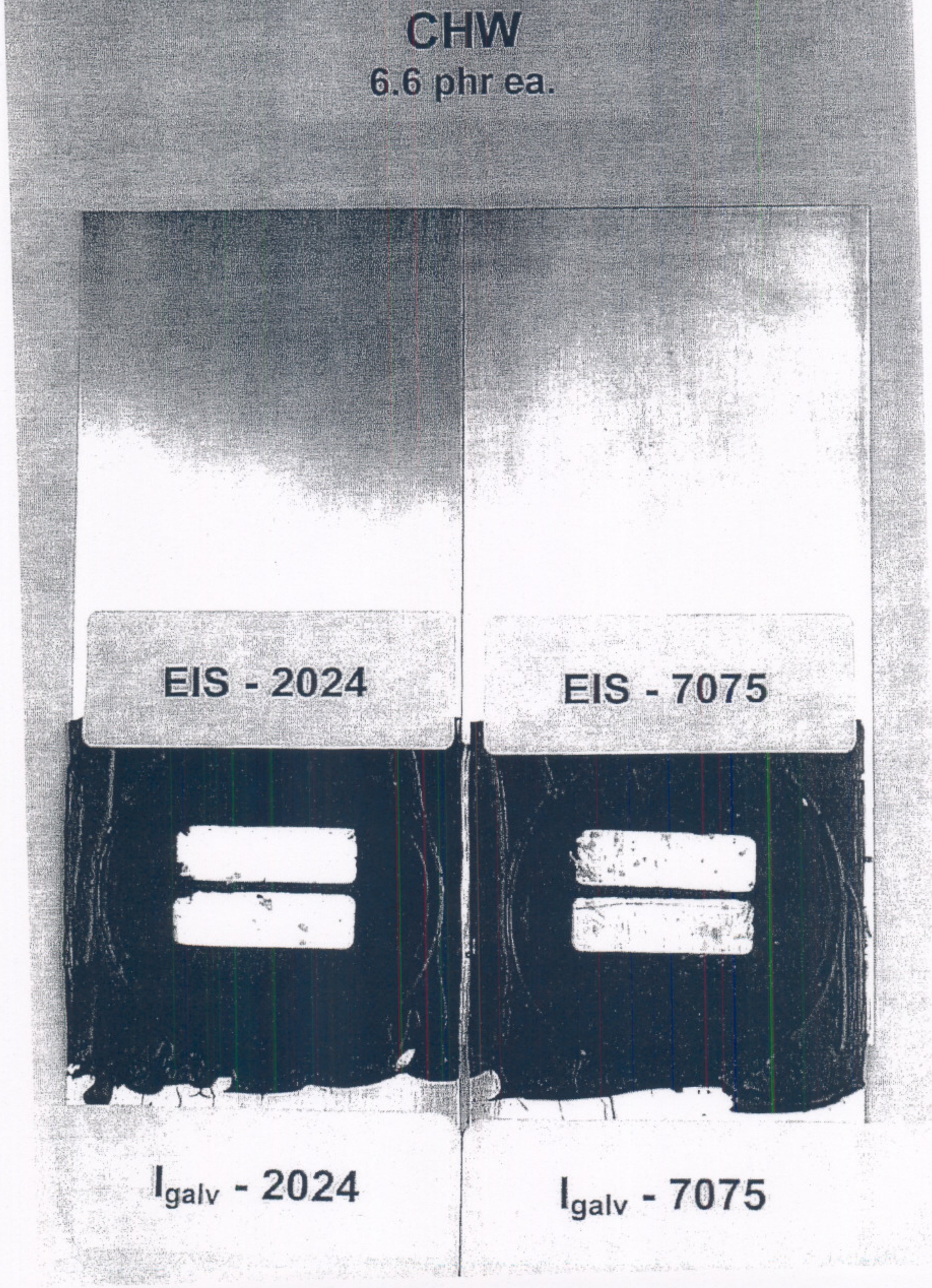


Figure 10: 5 phr Each of C, H, N, and W in Sealant:
Substrates after EIS and Igalv Testing

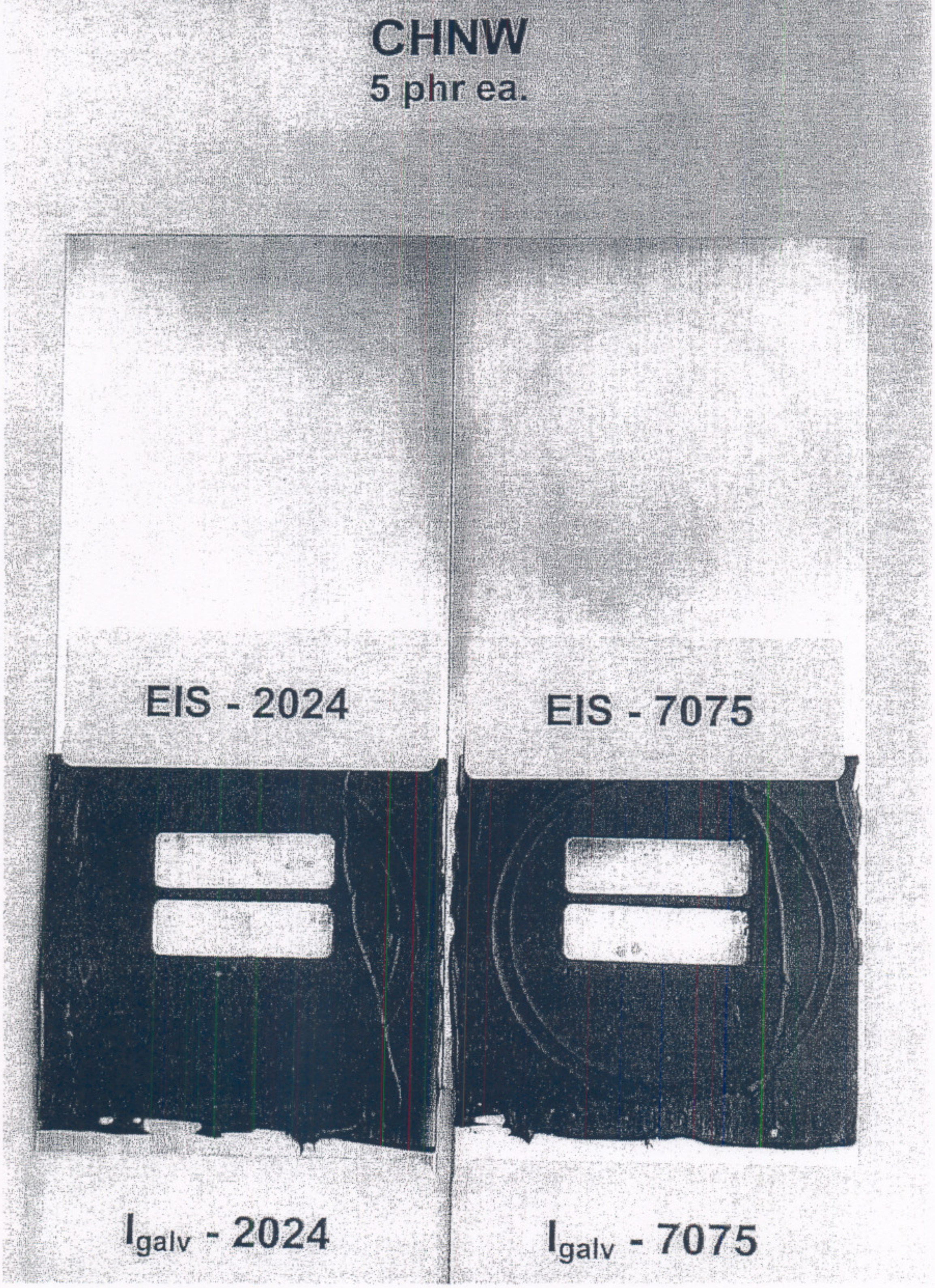


Figure 11: EIS Curves of Sealants with Single Inhibitors at 20 phr on 2024

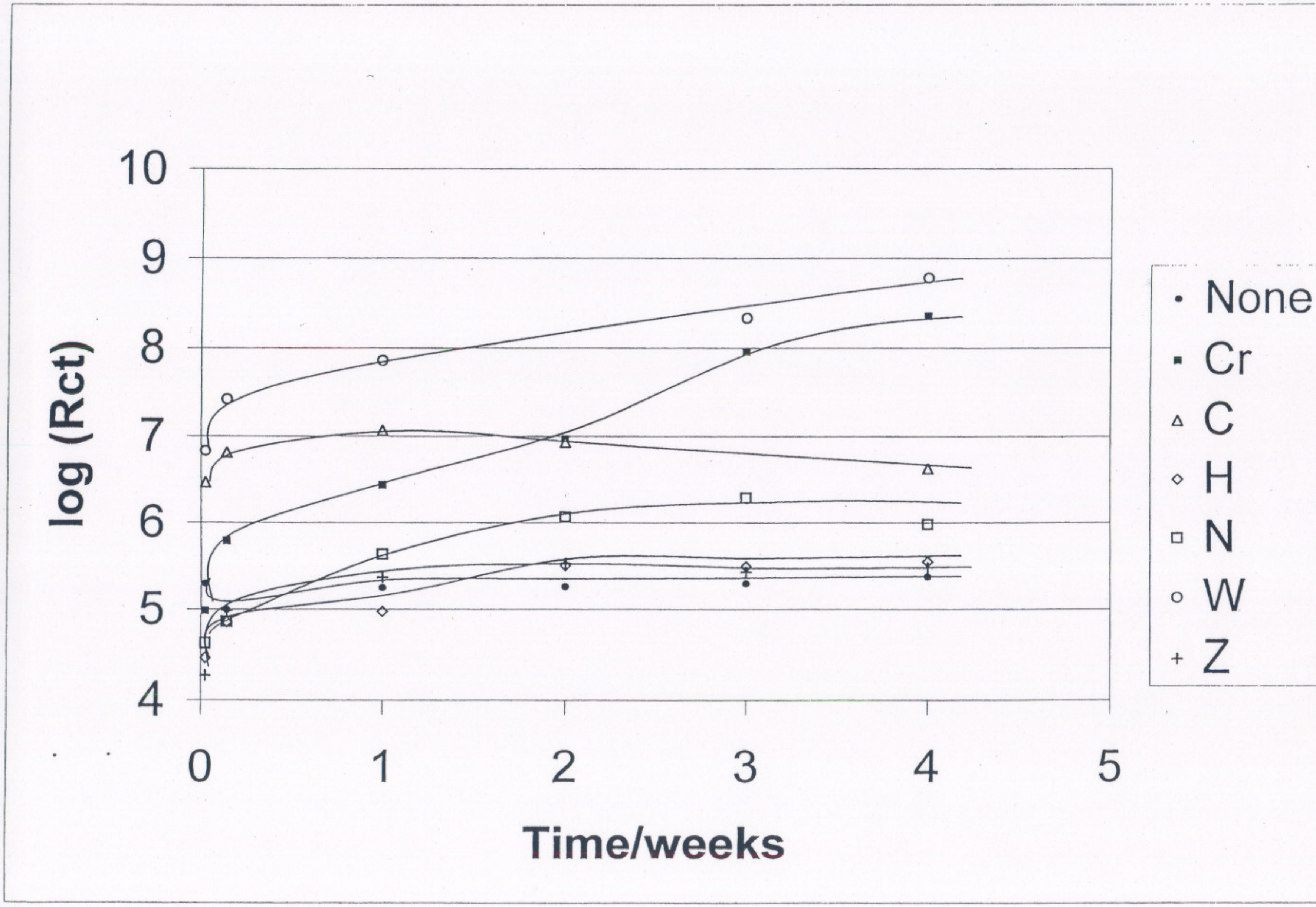


Figure 12: EIS Curves of Sealants with Single Inhibitors at 20 phr on 7075

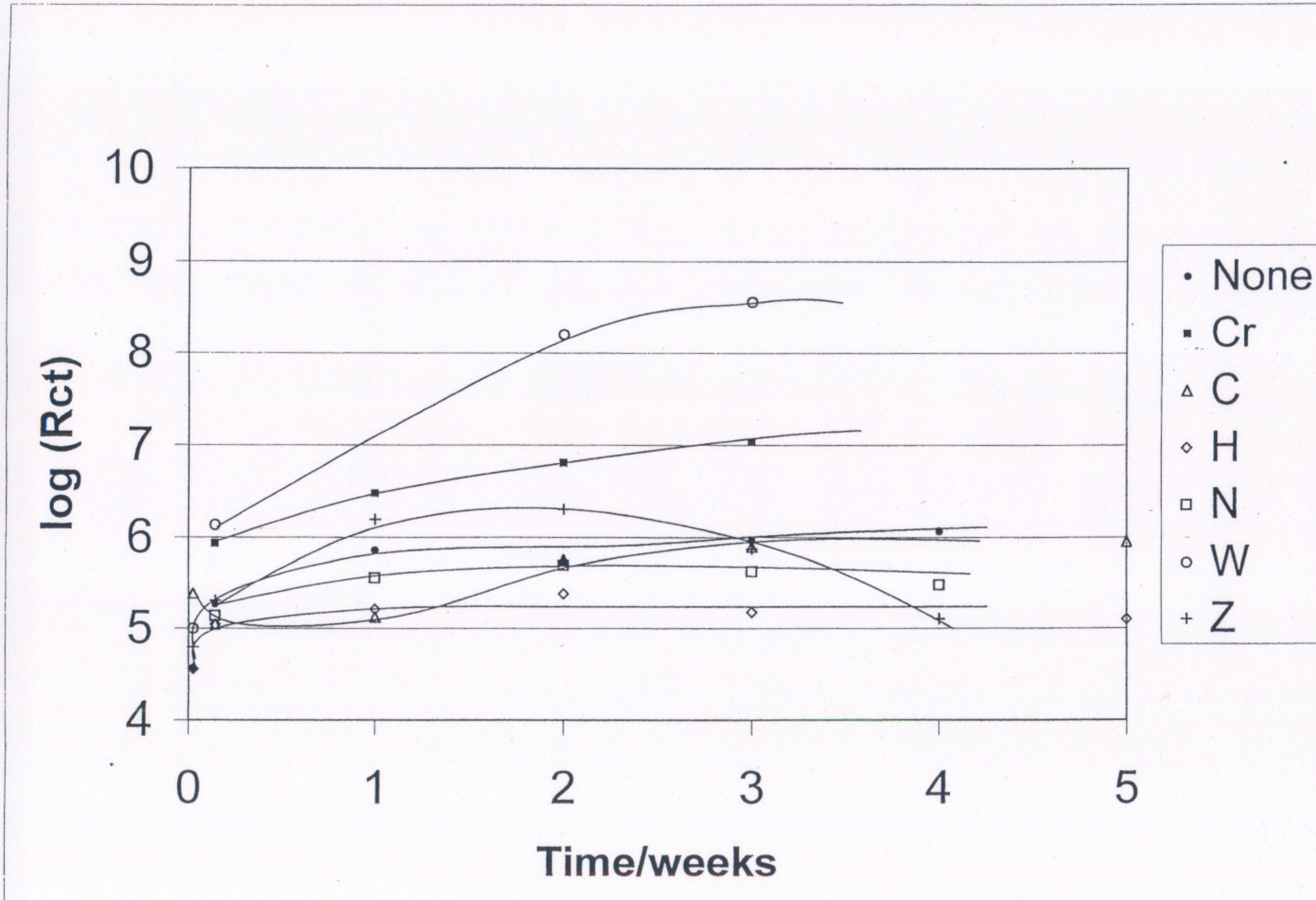


Figure 13: EIS Curves of Sealants with C, N, Z, and CNZ on 2024

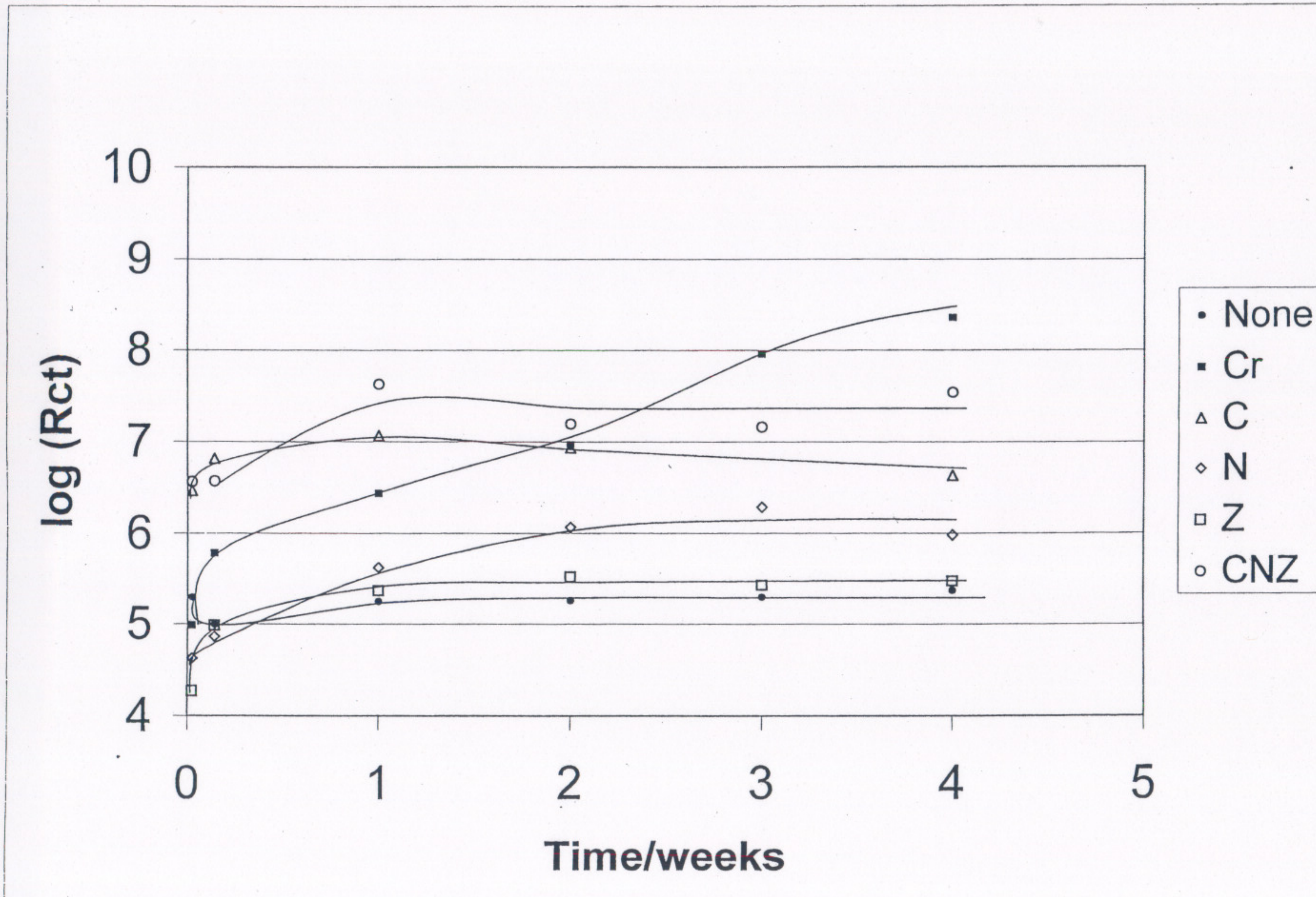


Figure 14: EIS Curves of Sealants with C, N, Z, and CNZ on 7075

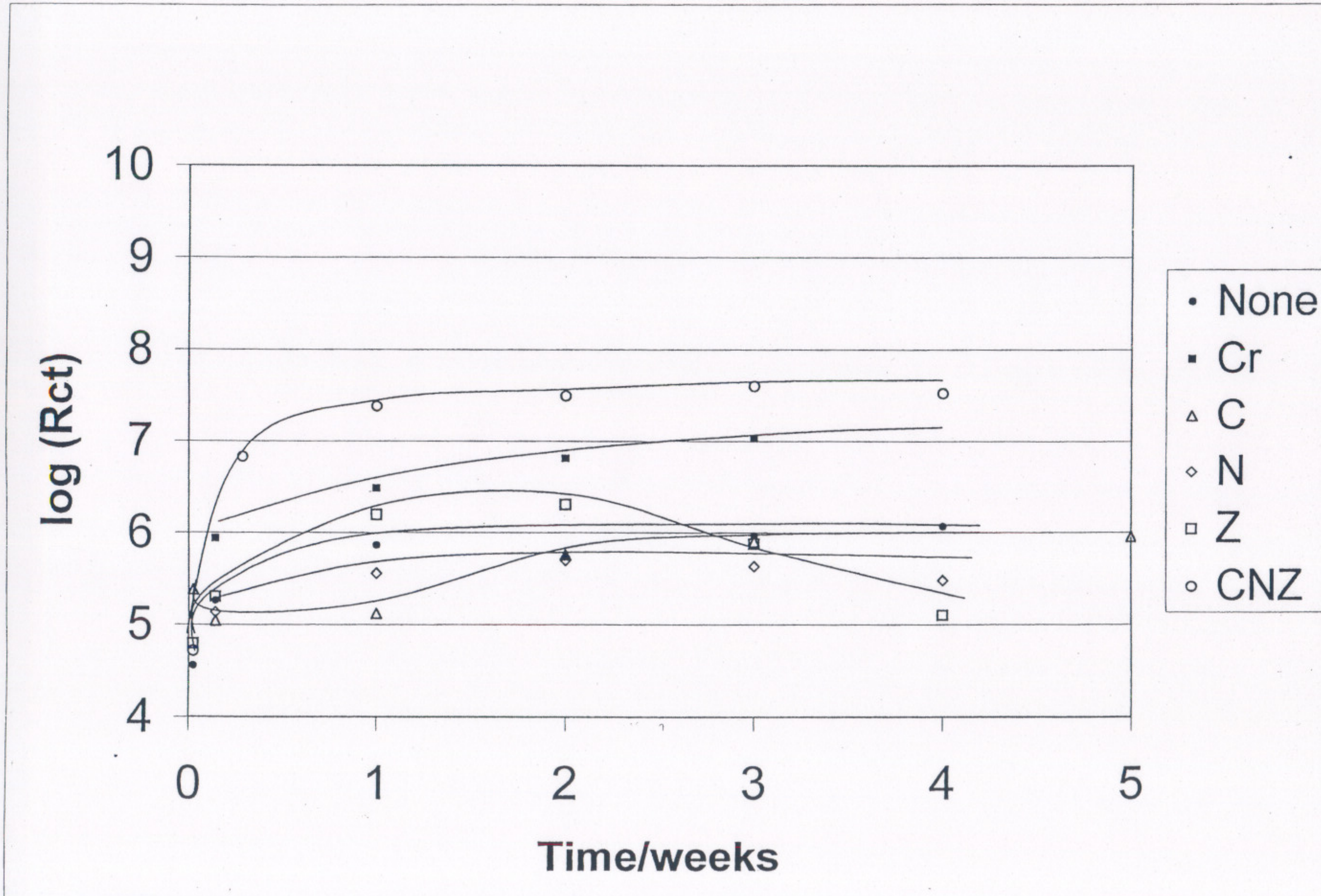


Figure 15: EIS Curves of Sealants with CHW, CNW, and CHNW on 2024

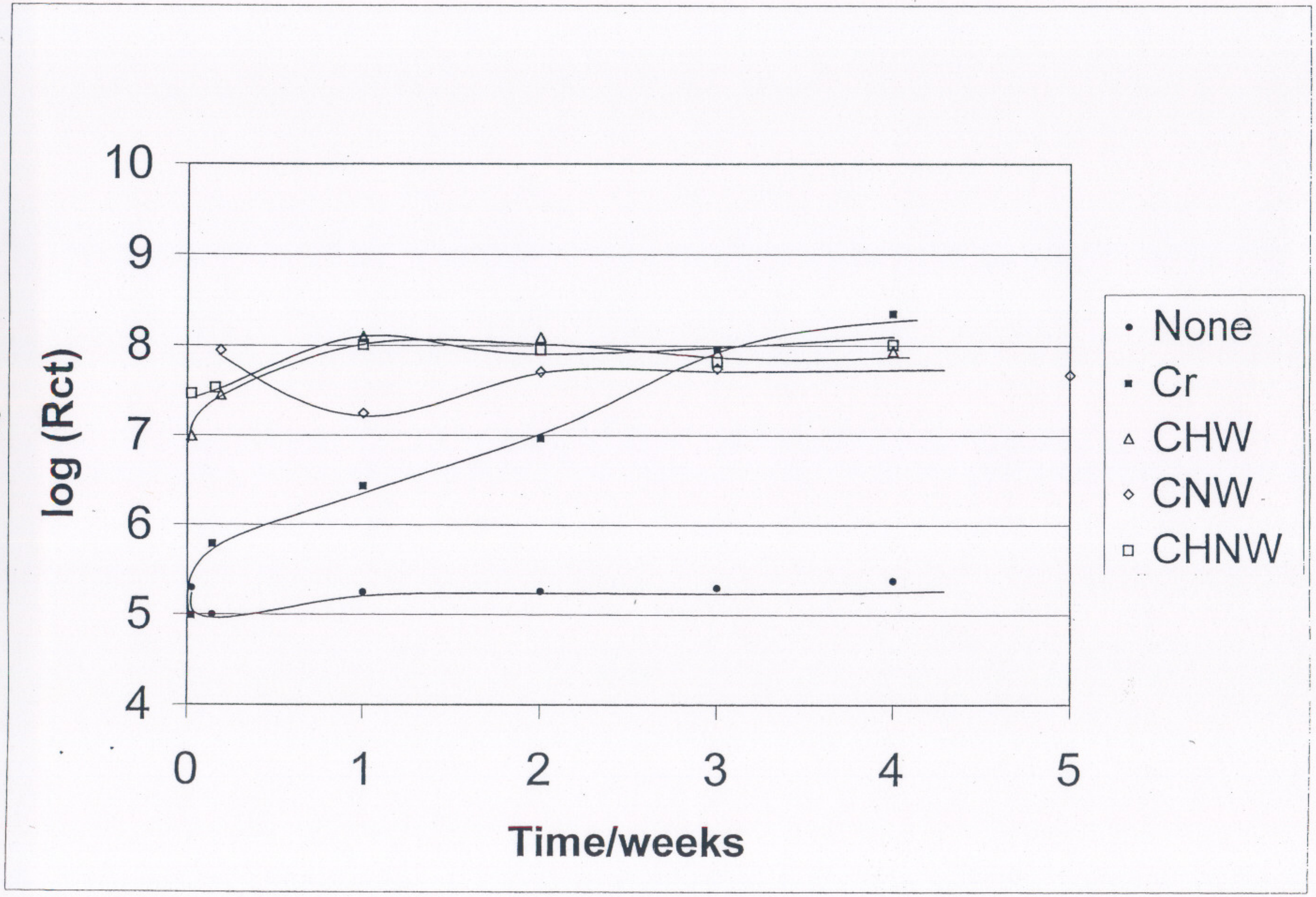
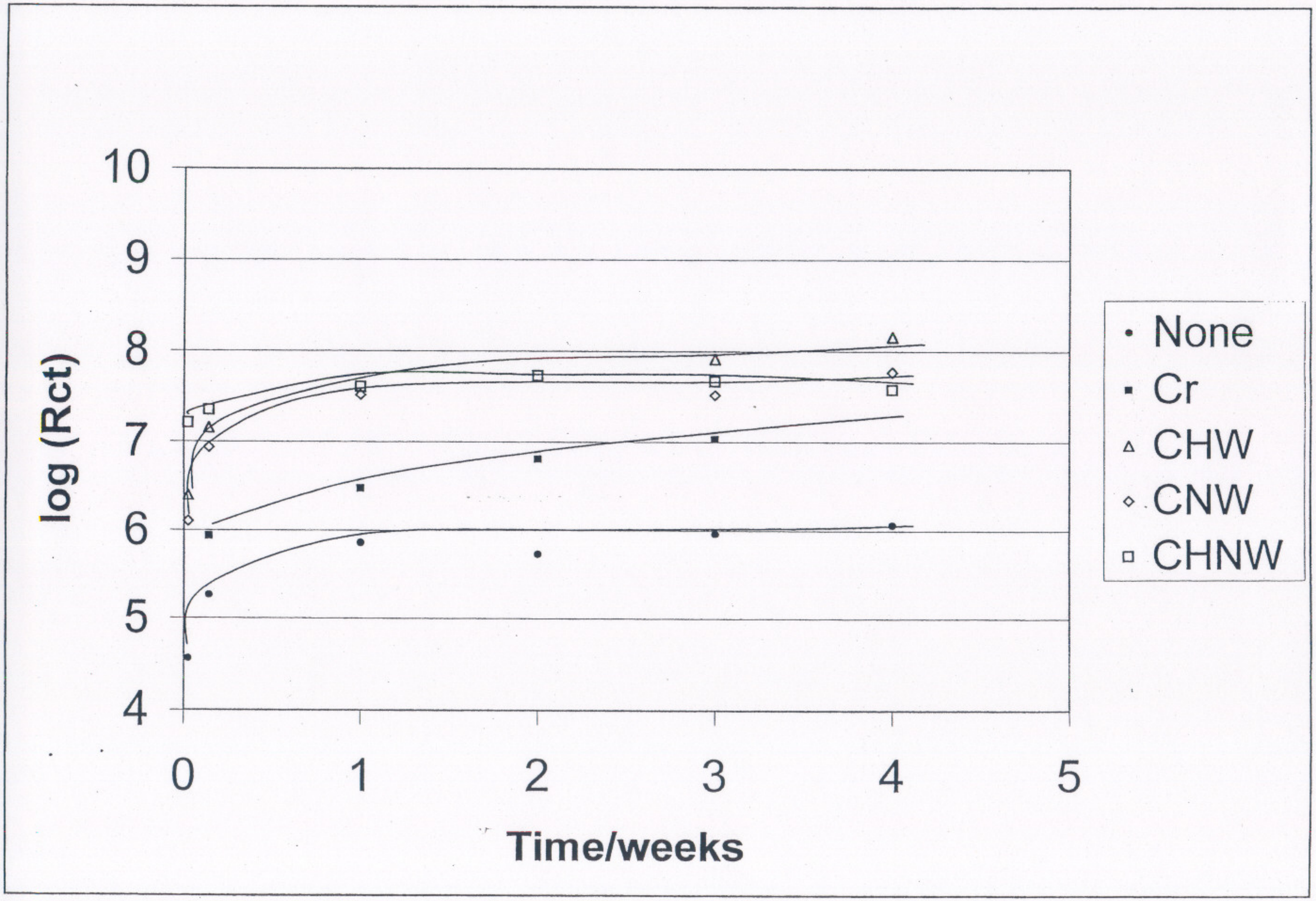


Figure 16: EIS Curves of Sealants with CHW, CNW, and CHNW on 7075



APPENDIX 1: Abbreviations Used

DEG-DVE	diethyleneglycol divinylether
Pluriol E-200 DVE	Pluriol E-200 divinylether
BD-DVE	butanediol divinylether
HD-DVE	hexanediol divinylether
Poly THF DVE	poly THF divinylether
TEG-DVE	triethyleneglycol divinylether
EG-DVE	ethyleneglycol divinylether
CHVE	cyclohexanedimethanol divinylether
di-PG-DVE	dipropyleneglycol divinylether
ECHDT	ethylcyclohexanedithiol
DMDS	dimercaptodiethylsulfide
DMDO	1,8-dimercapto-3,6-dioxaoctane
HDT	1,6-hexanedithiol
DPDM	dipentene dimercaptan
DGE	diglycidylether
TGE	triglycidylether
BD-DGE	butanediol diglycidylether
Bis A DGE	bisphenol A diglycidylether
Bis F DGE	bisphenol F diglycidylether
CHDM DGE	cyclohexanedimethanol diglycidylether
NPG-DGE	neopentyl diglycidylether
TMP-TGE	trimethylolpropane triglycidylether

APPENDIX B

U.S. ARMY RESEARCH LABORATORY TEST REPORT

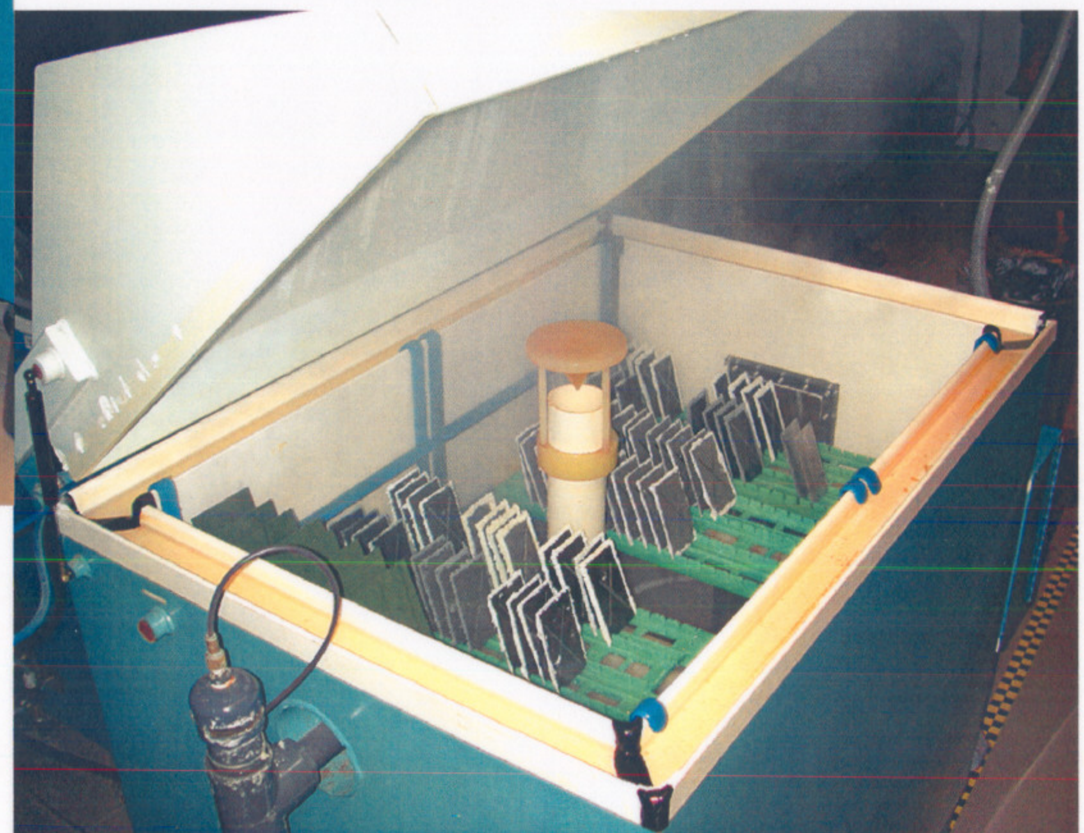
Corrosion Inhibiting Sealants

Brian E. Placzankis
U.S. Army Research Laboratory
Aberdeen Proving Ground

SAE AMS G9, Aerospace Sealing Committee Meeting
Royal Scandinavian Hotel, Solvang, CA

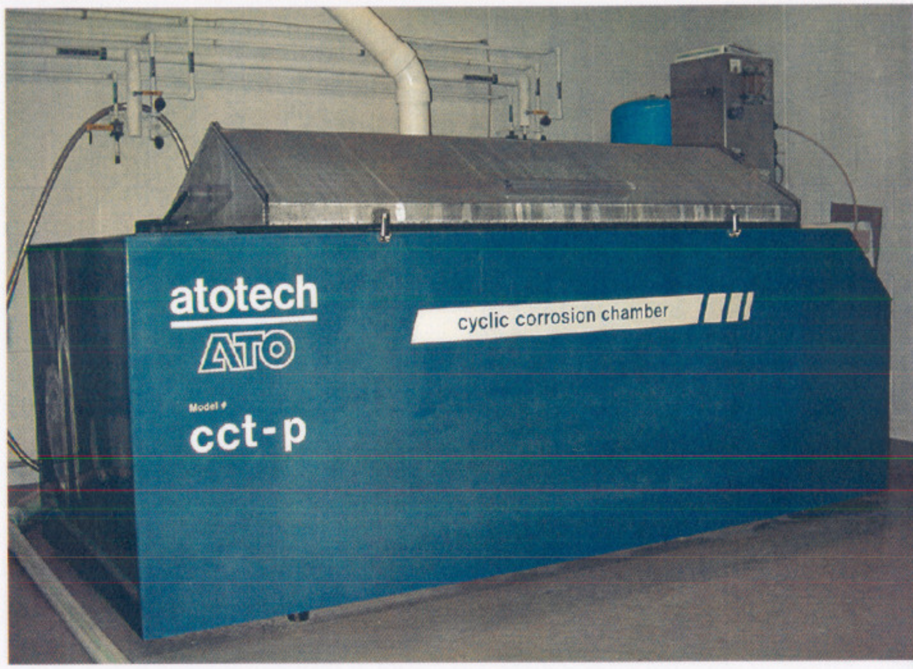
ASTM B 117 (Saltfog)

- Standard Wet Bottom ASTM B 117 Saltfog Chamber



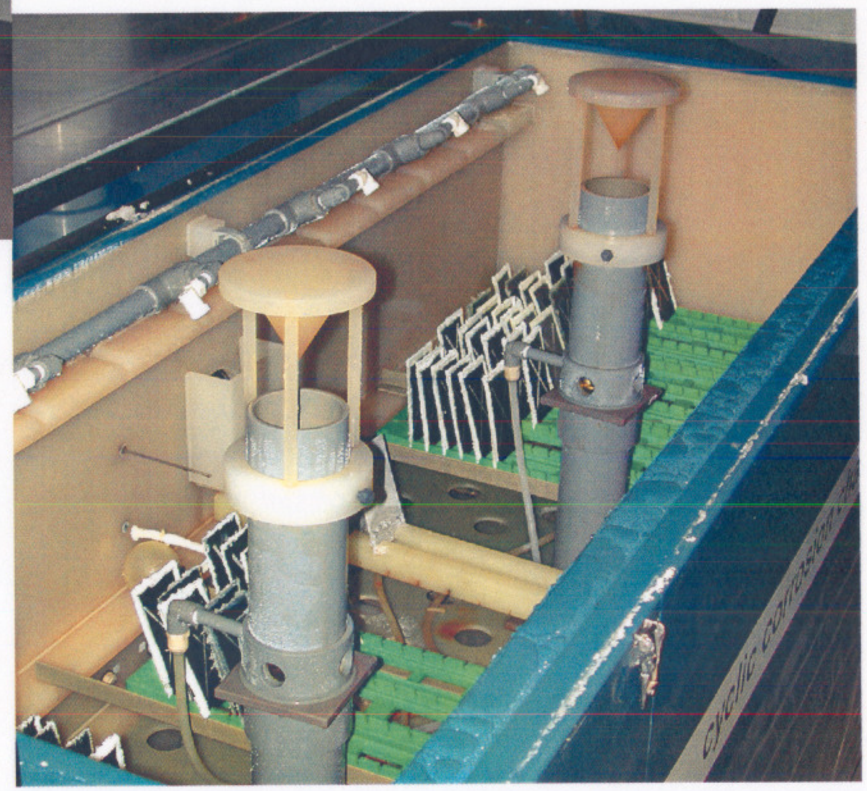
- Interior view of test in progress
- High resolution scans performed weekly for all test coupons
- Images on CD ROM

ASTM G 85 A5 (Prohesion)

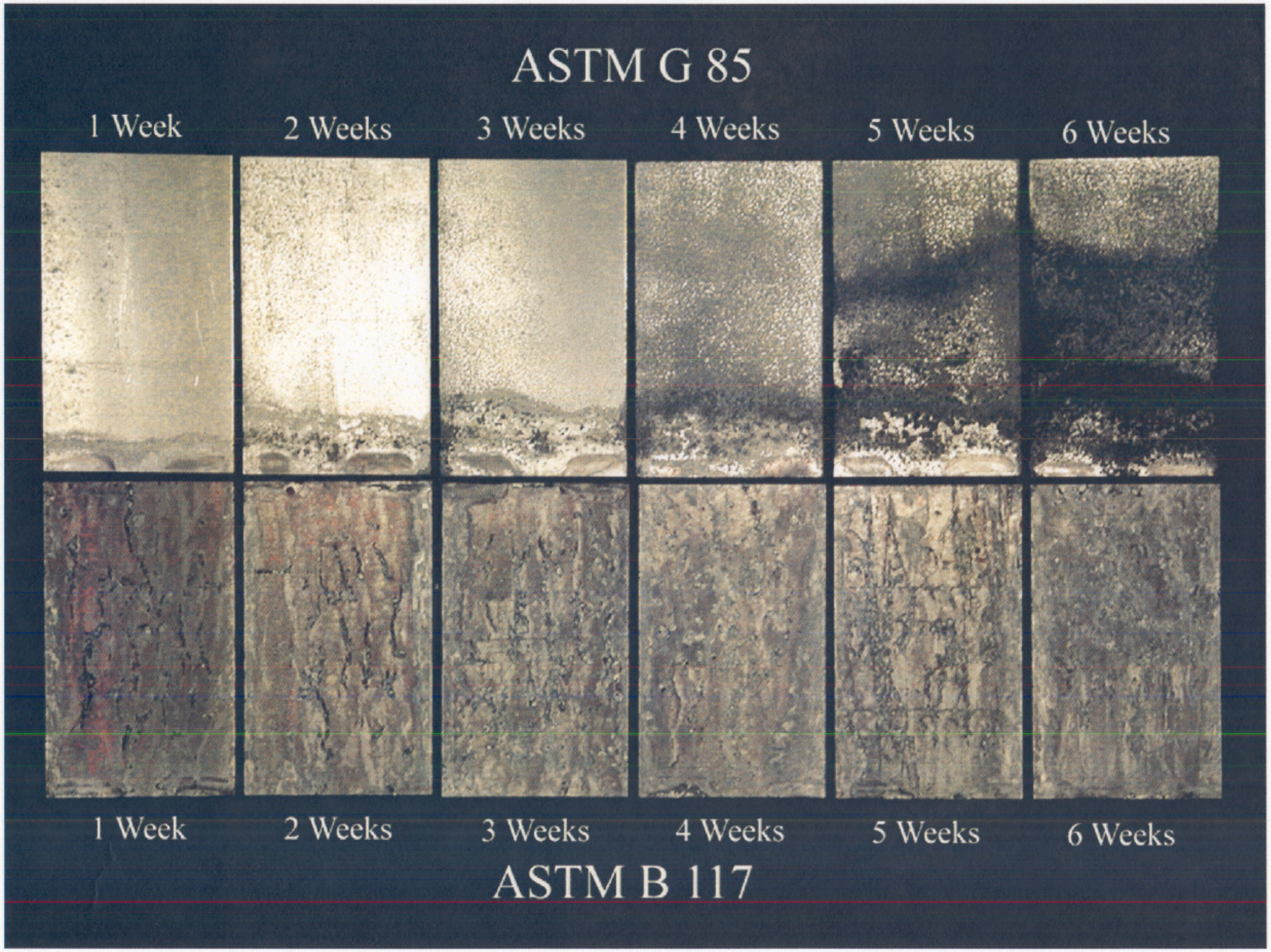


- Atotech Chamber Programed for ASTM G 85 A5 (Prohesion)

- Interior view of test in progress
- High resolution scans performed weekly for all test coupons
- Images on CD ROM

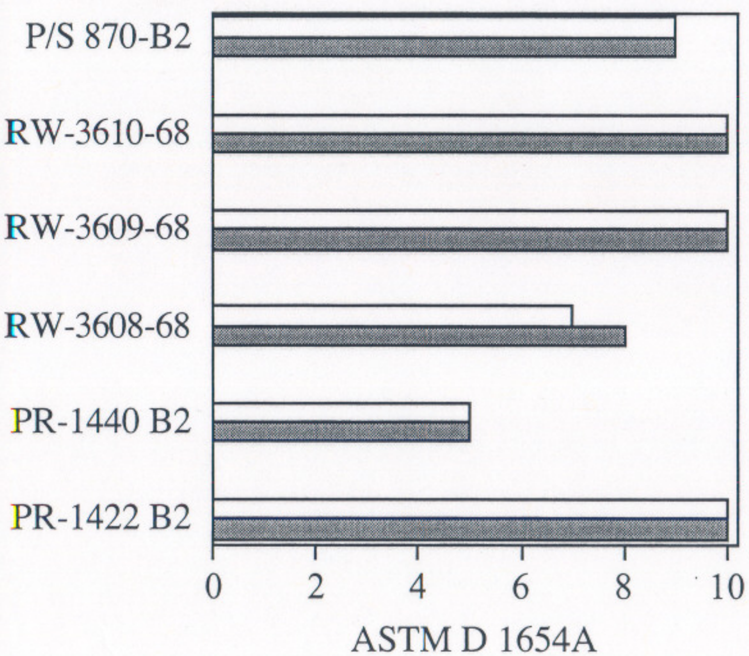


Complete Accelerated Exposure Intervals for AMS 4045 Bare Test Coupons

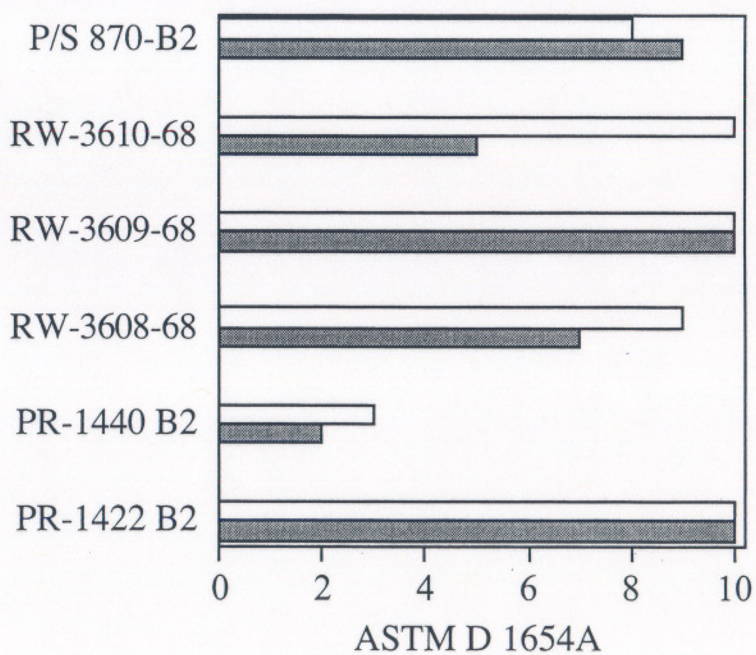


Saltfog Corrosion

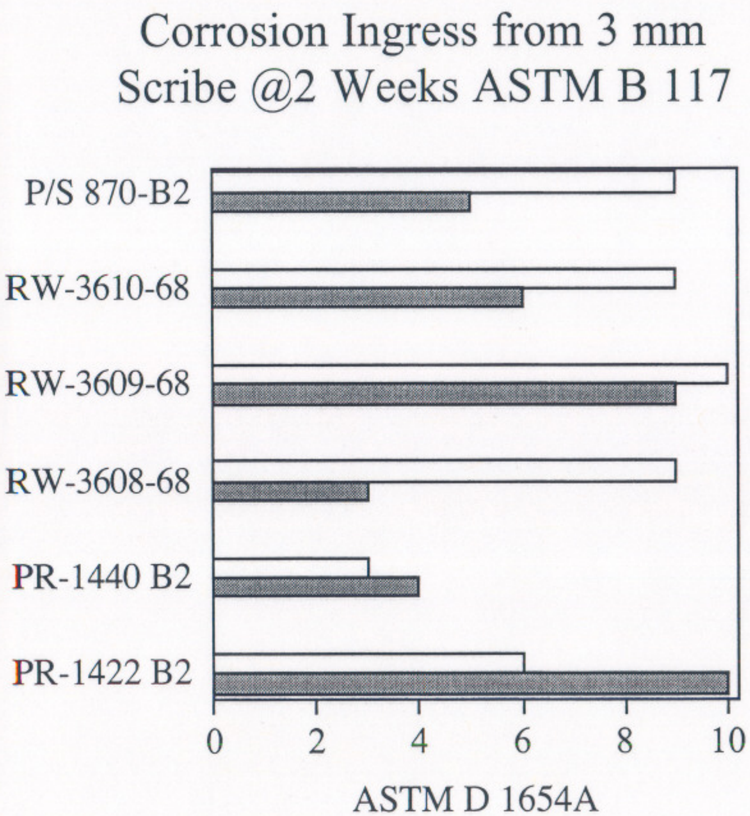
Corrosion Ingress from 3 mm Scribe @1 Week ASTM B 117

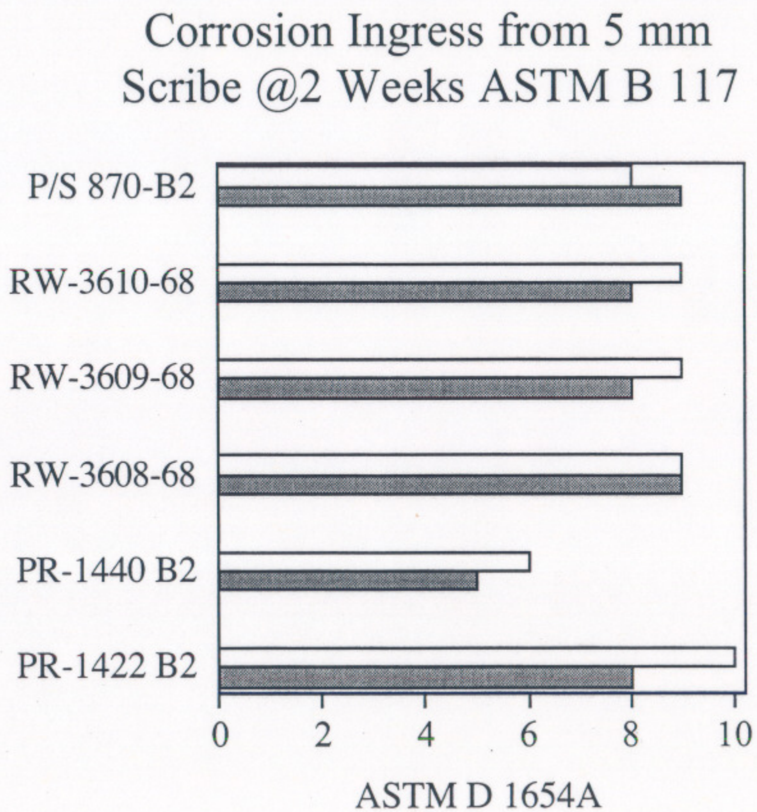


Corrosion Ingress from 5 mm Scribe @1 Week ASTM B 117



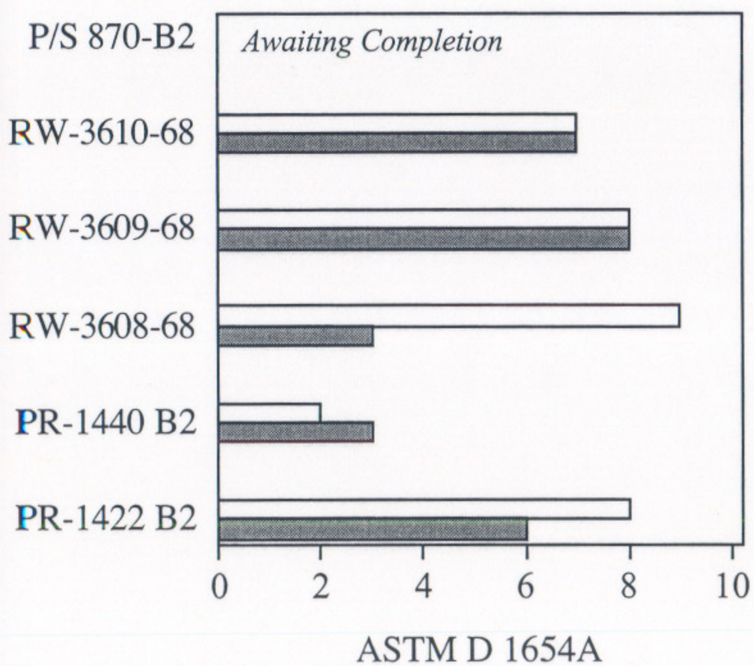
Saltfog Corrosion



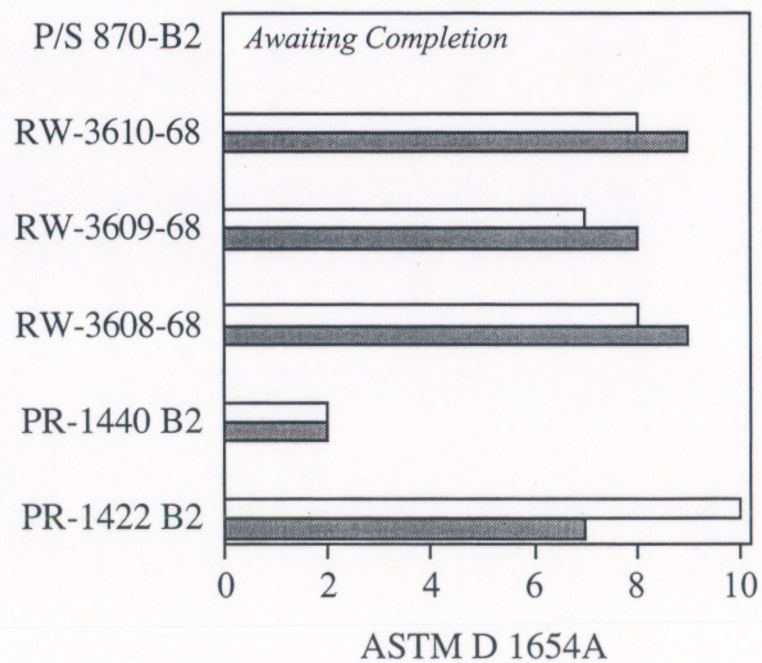


Saltfog Corrosion

Corrosion Ingress from 3 mm Scribe @3 Weeks ASTM B 117

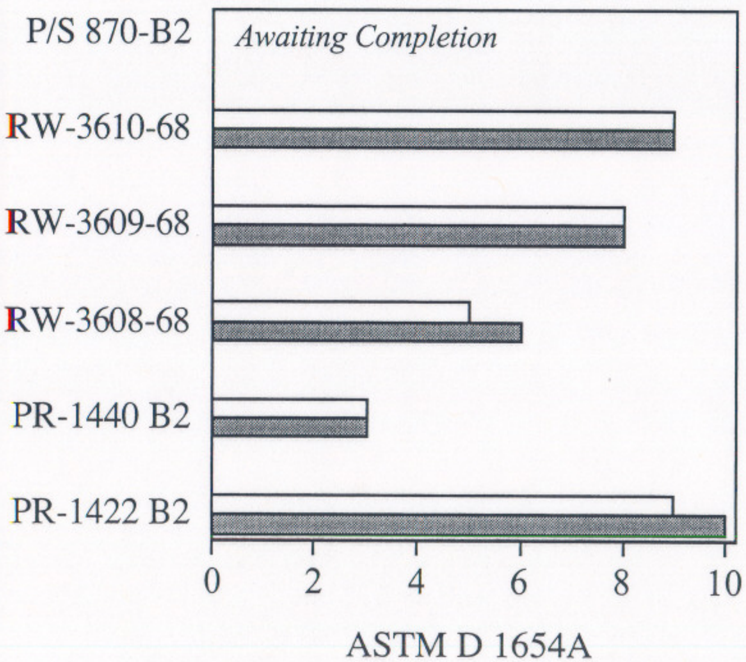


Corrosion Ingress from 5 mm Scribe @3 Weeks ASTM B 117

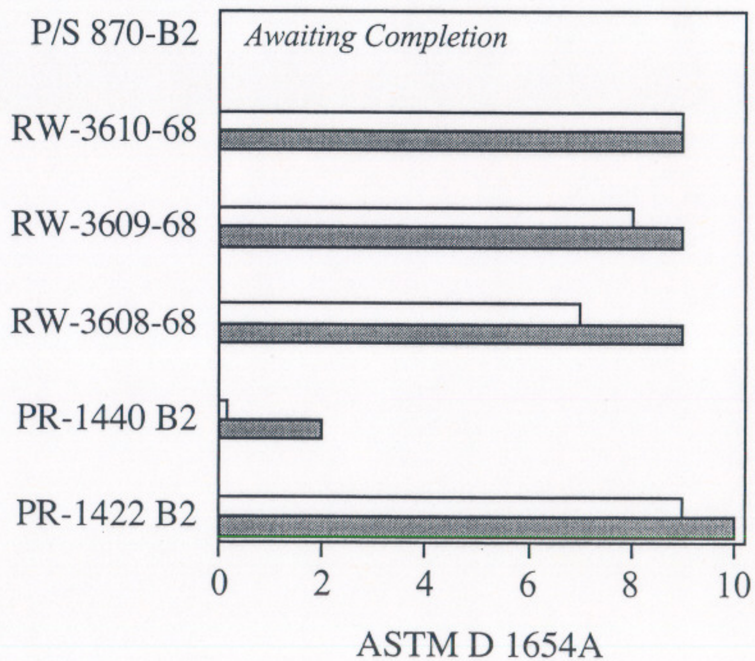


Saltfog Corrosion

Corrosion Ingress from 3 mm Scribe @4 Weeks ASTM B 117

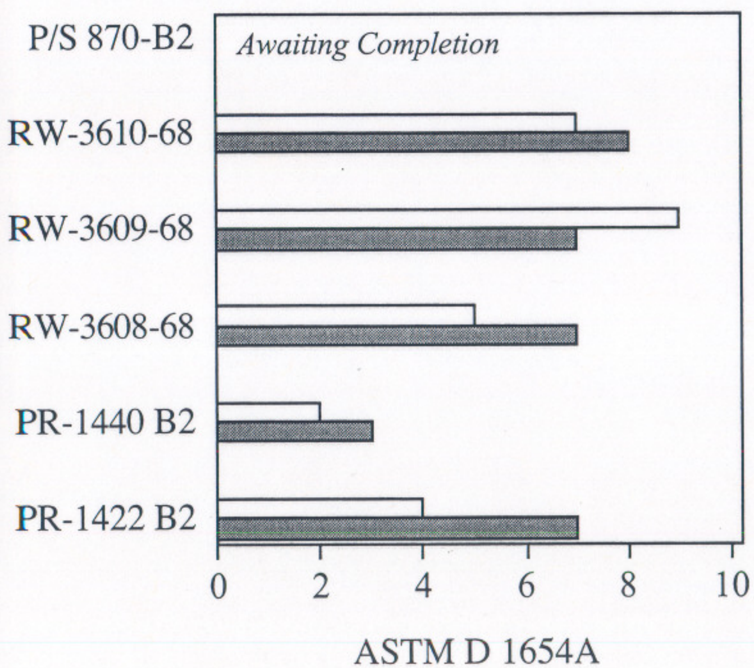


Corrosion Ingress from 5 mm Scribe @4 Weeks ASTM B 117

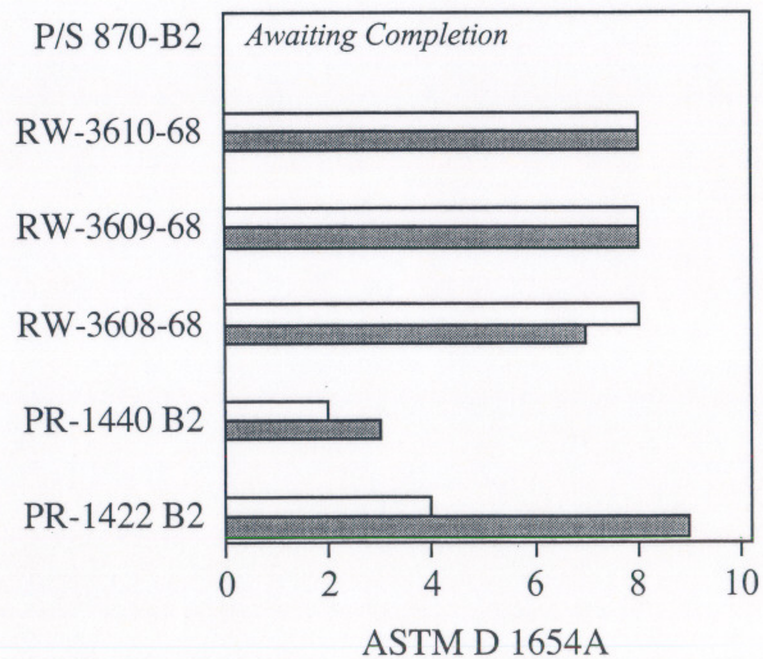


Saltfog Corrosion

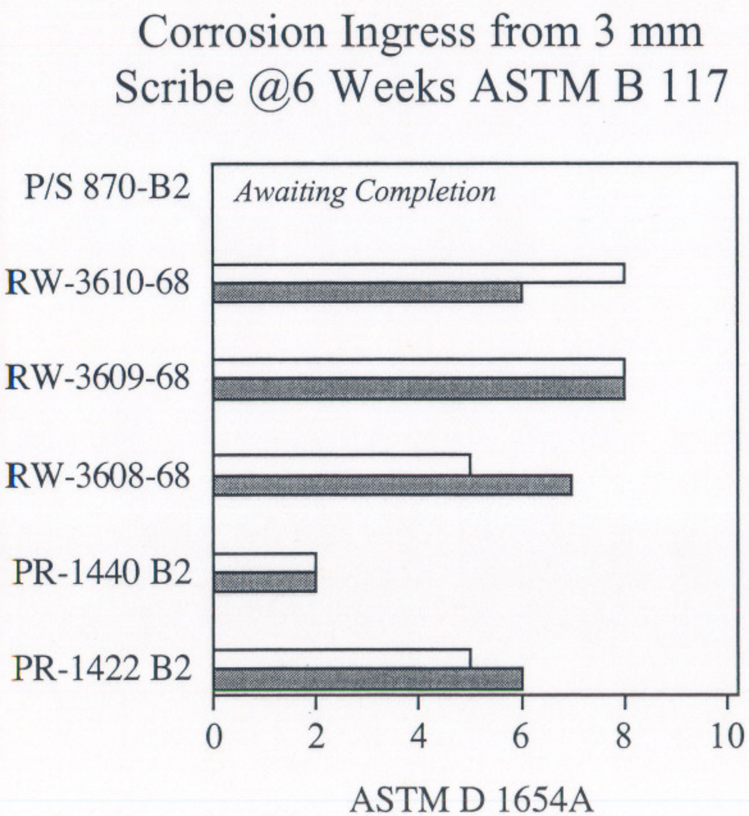
Corrosion Ingress from 3 mm Scribe @5 Weeks ASTM B 117

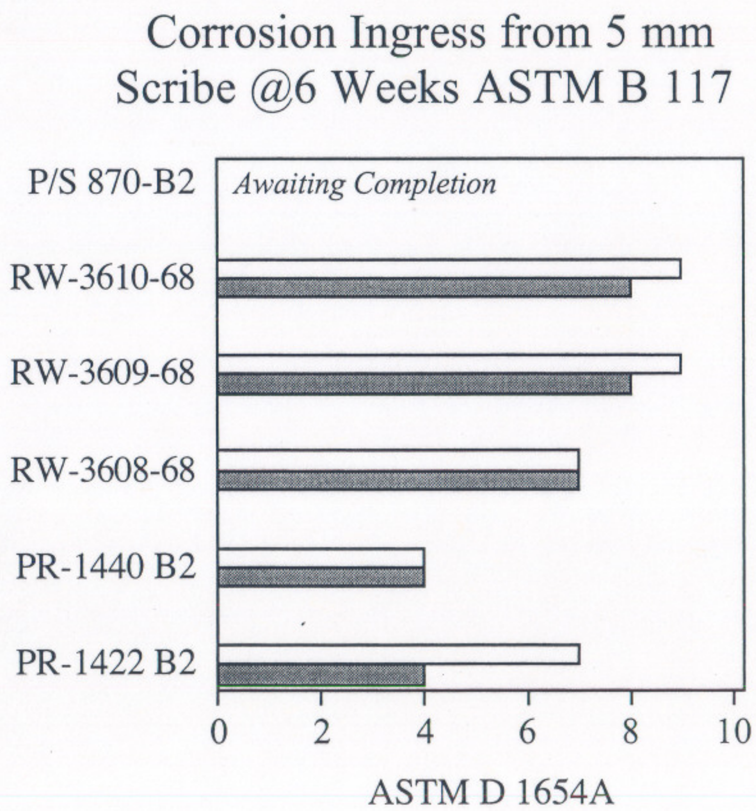


Corrosion Ingress from 5 mm Scribe @5 Weeks ASTM B 117



Saltfog Corrosion





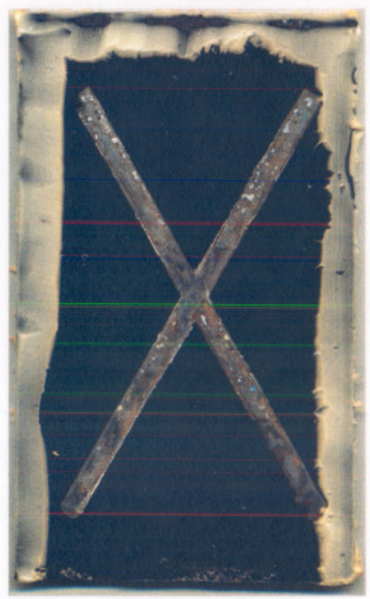
Saltfog Corrosion @6 Weeks

Bare AMS 4045

PR-1422 B2

PR-1440 B2

RW-3608-68



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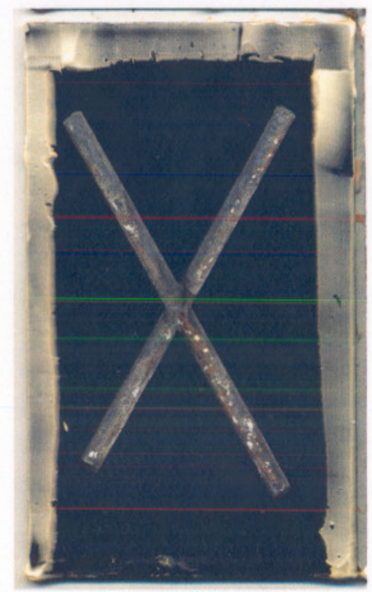
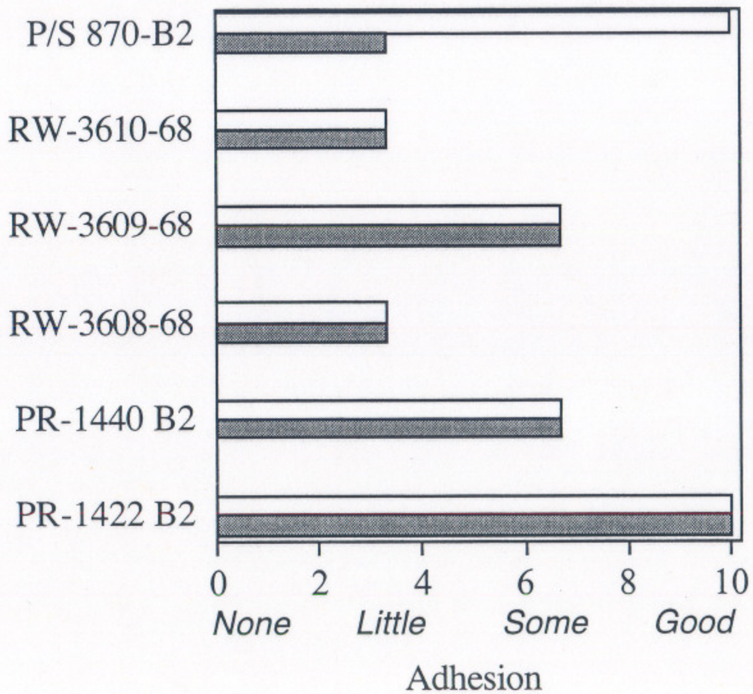


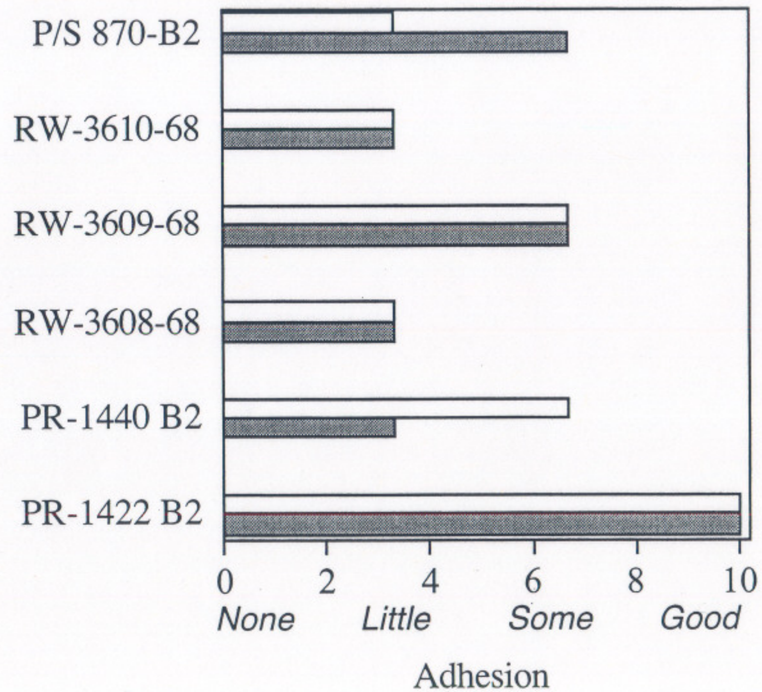
RW 3610-68

Saltfog Adhesion

3 mm Scribe Adhesion
@1 Week ASTM B 117

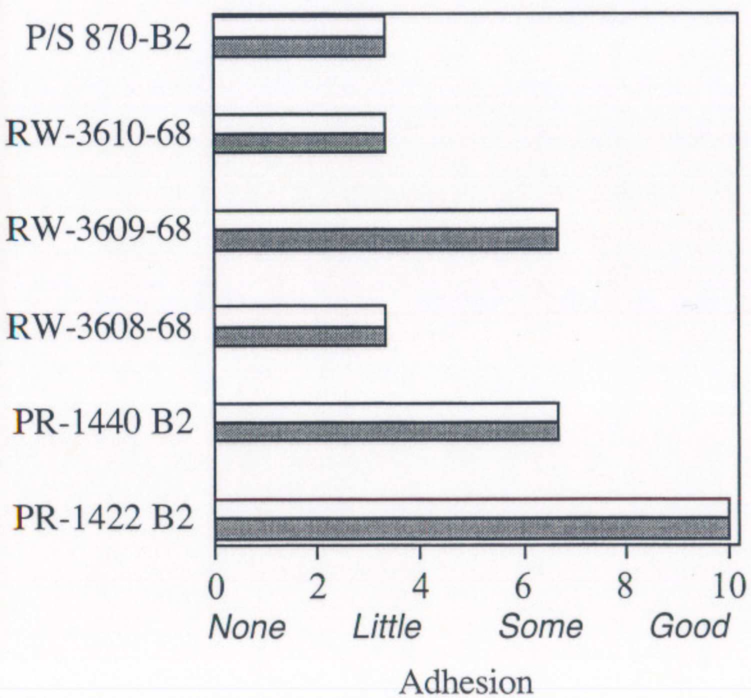


5 mm Scribe Adhesion
@1 Week ASTM B 117



Saltfog Adhesion

3 mm Scribe Adhesion
@2 Weeks ASTM B 117



5 mm Scribe Adhesion
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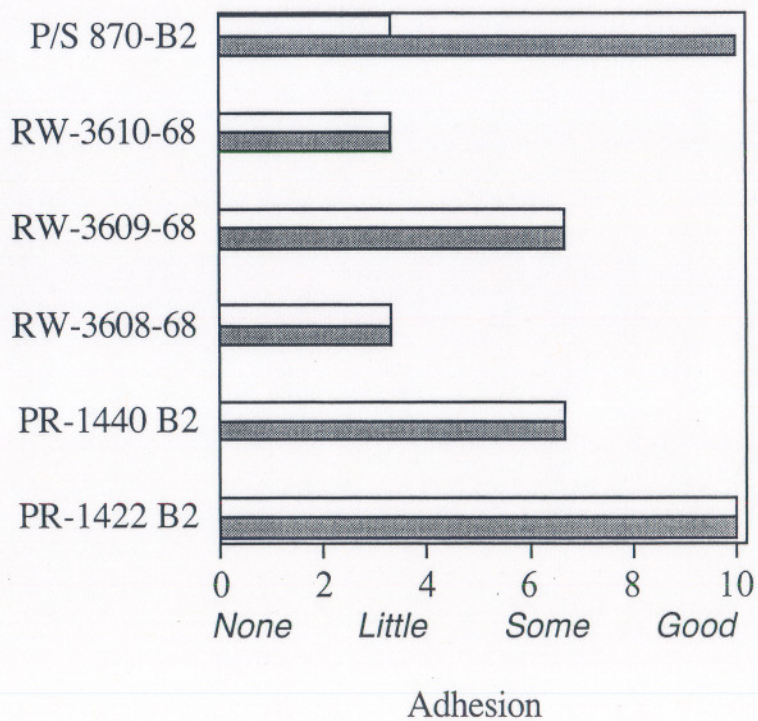
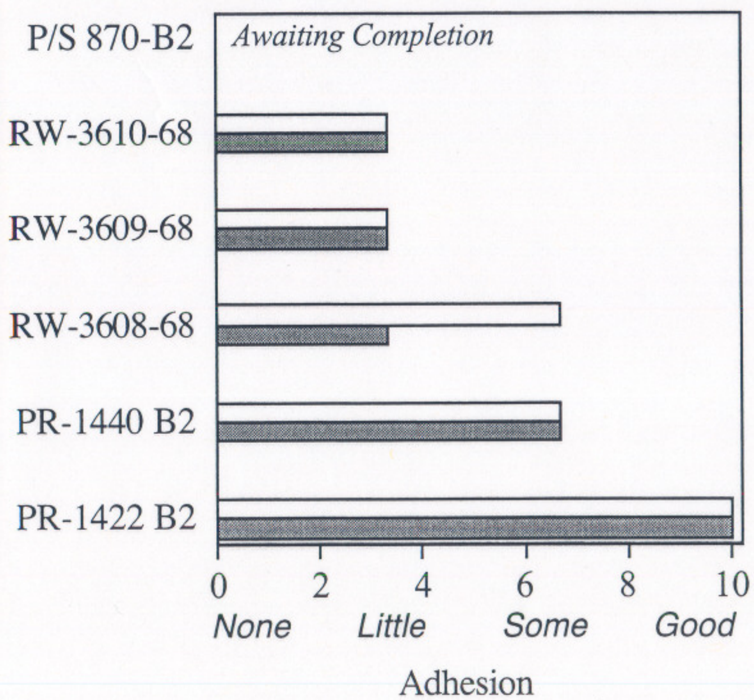


Saltfog Adhesion

3 mm Scribe Adhesion
@3 Weeks ASTM B 117



5 mm Scribe Adhesion
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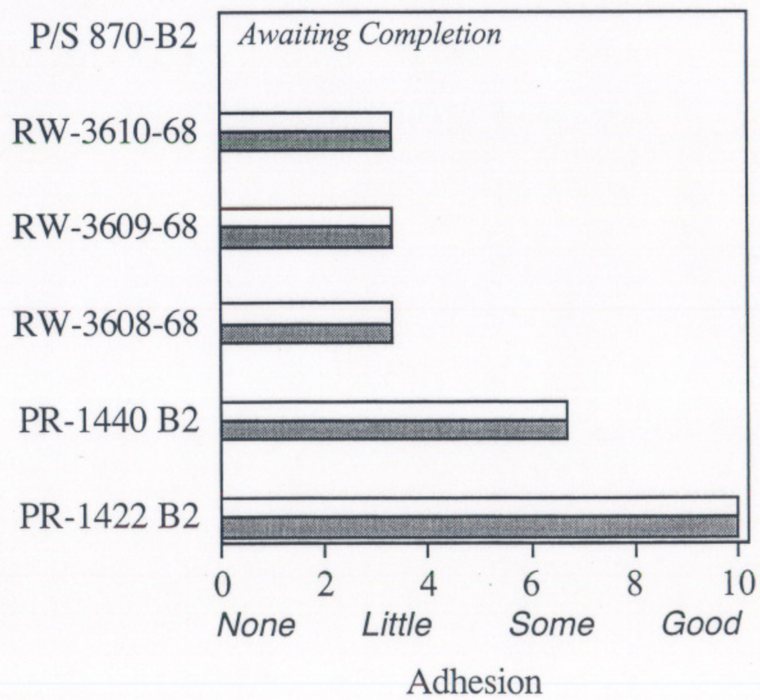
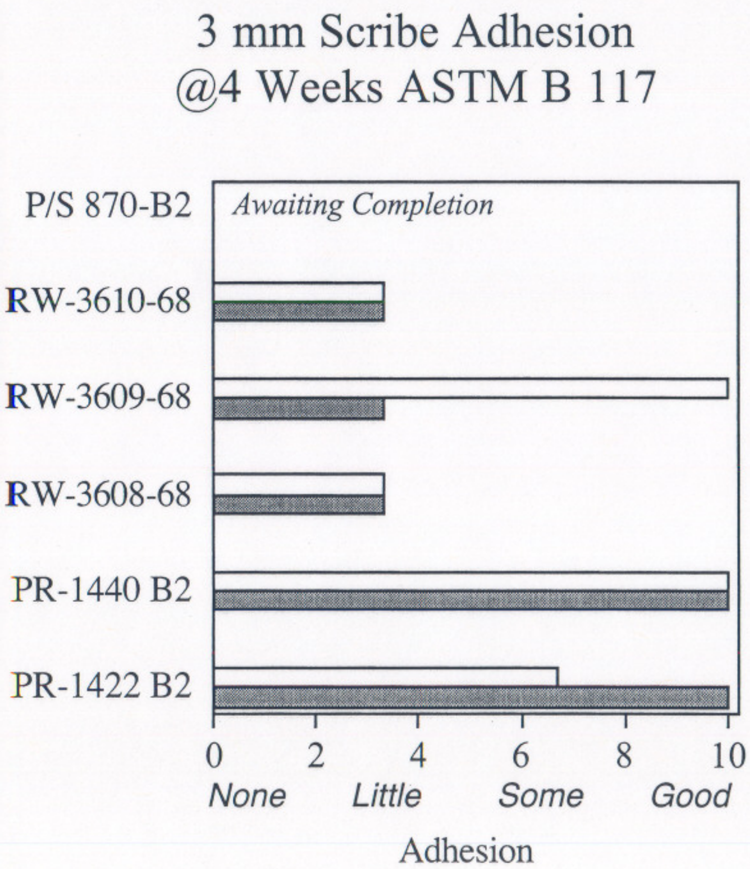
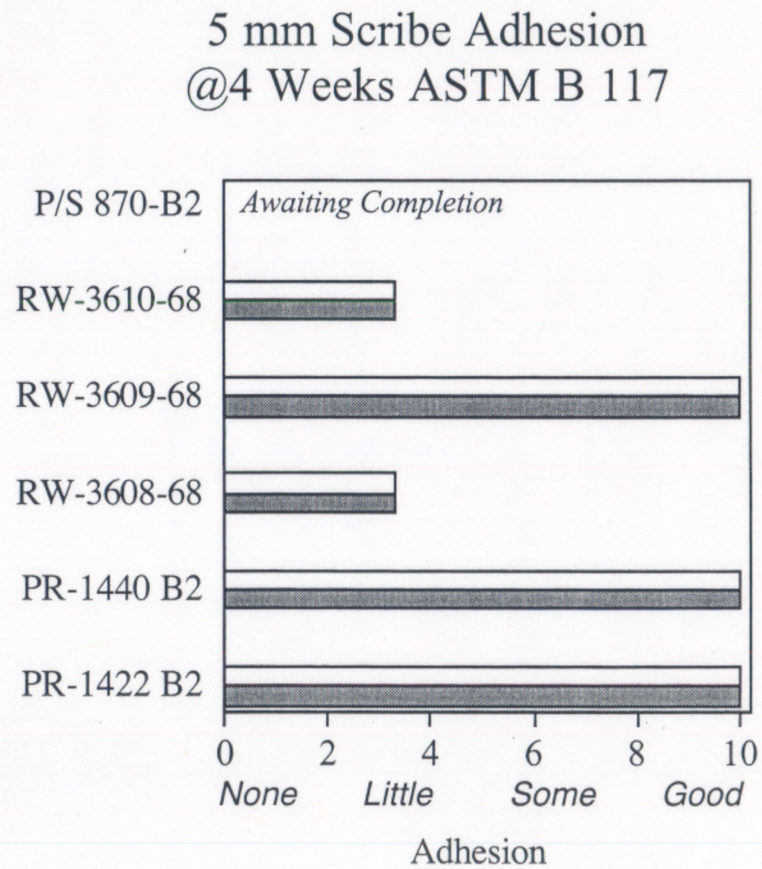


Saltfog Adhesion





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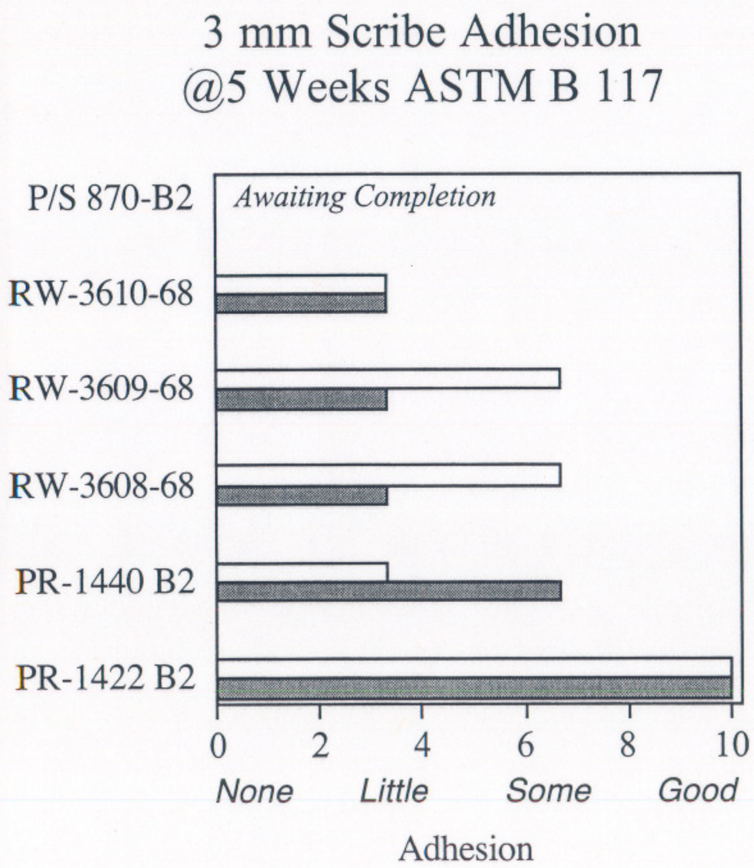

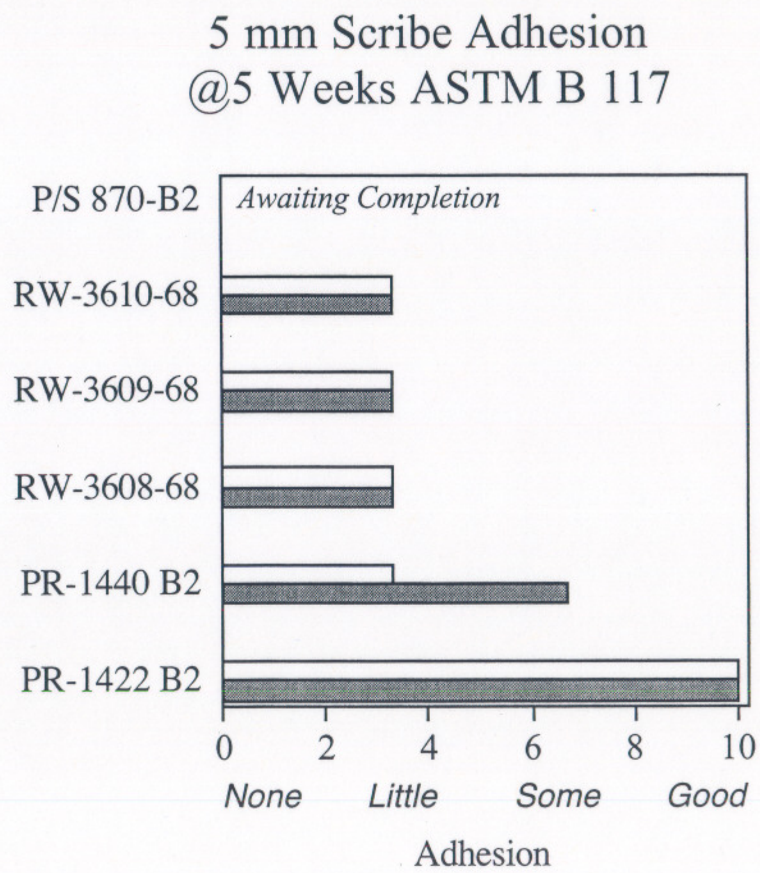

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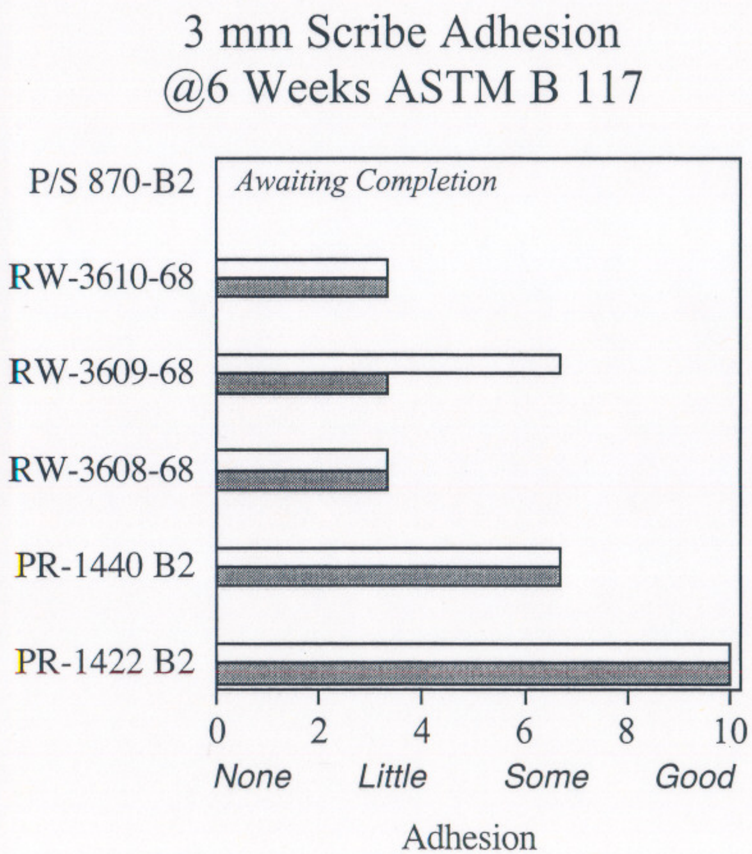
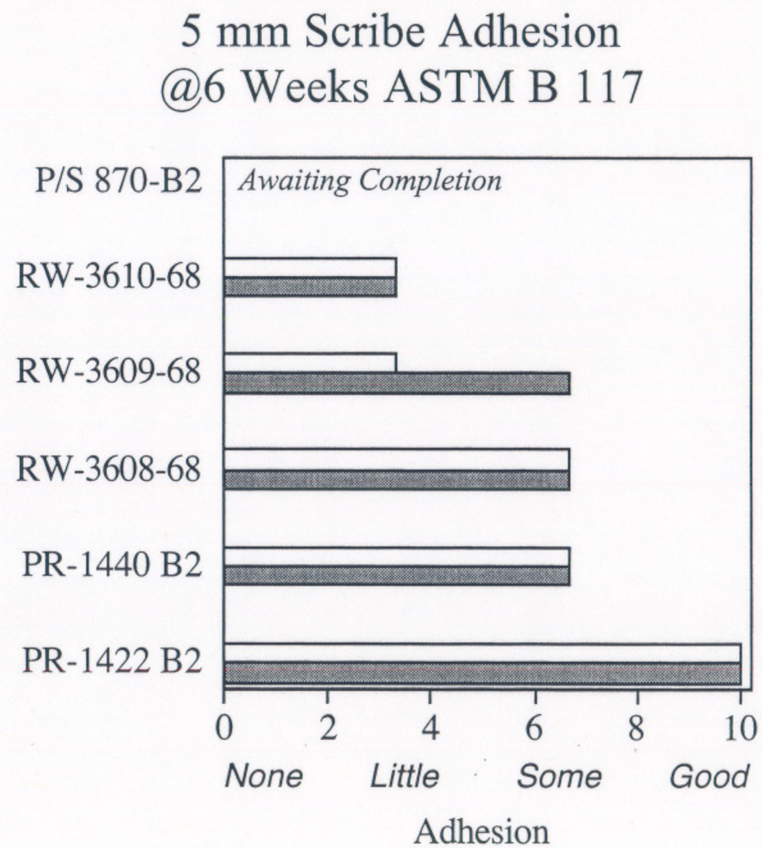
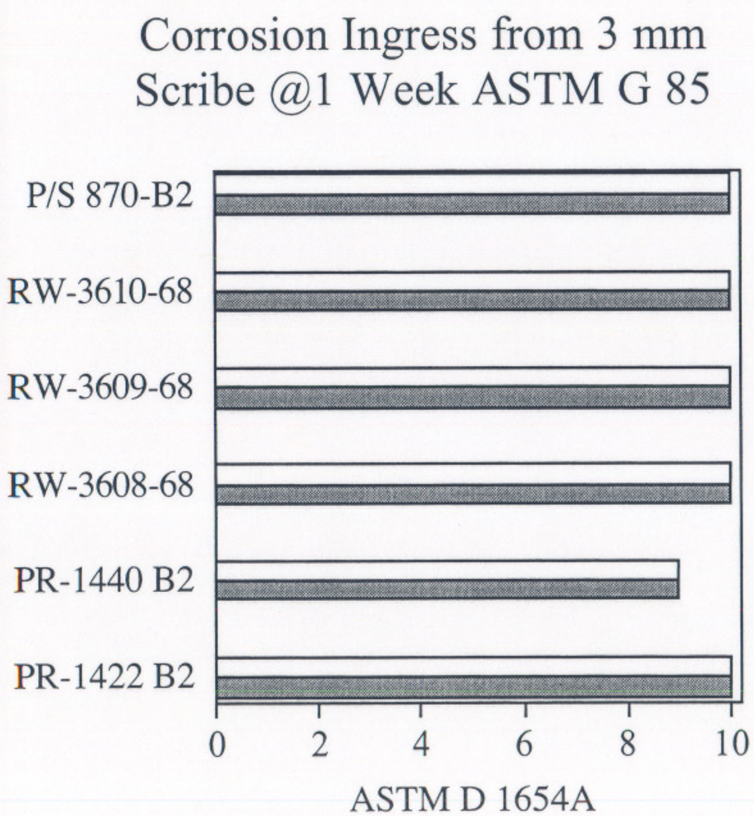
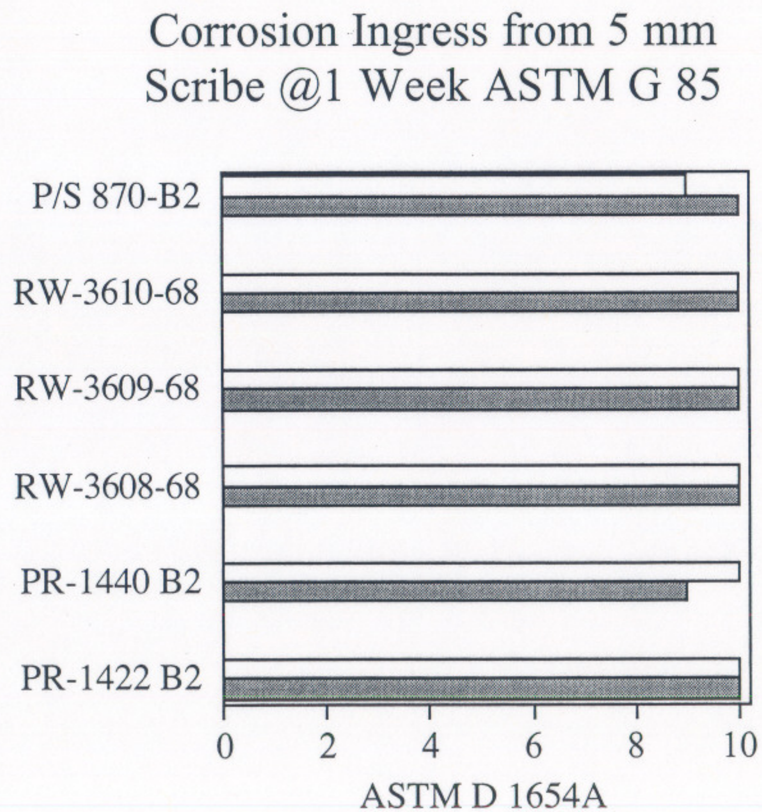




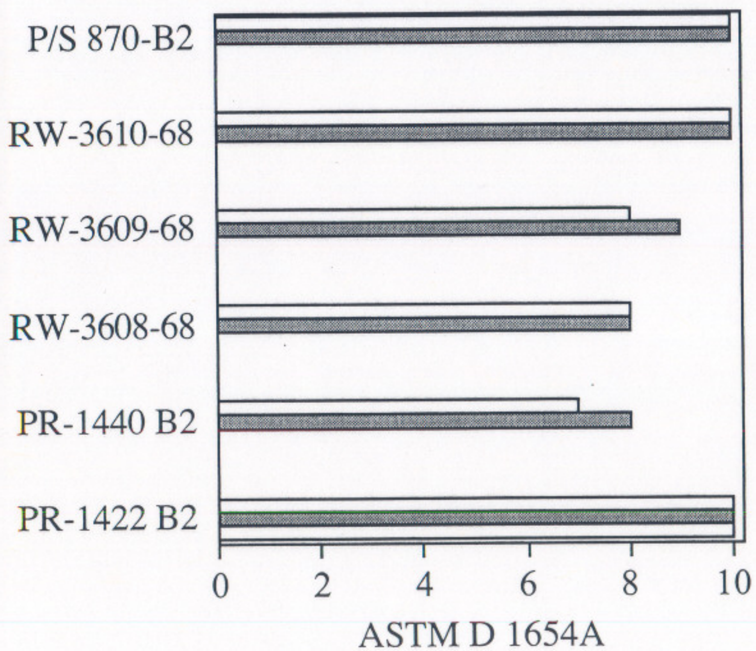
ASTM G 85 A5 (Prohesion) Corrosion



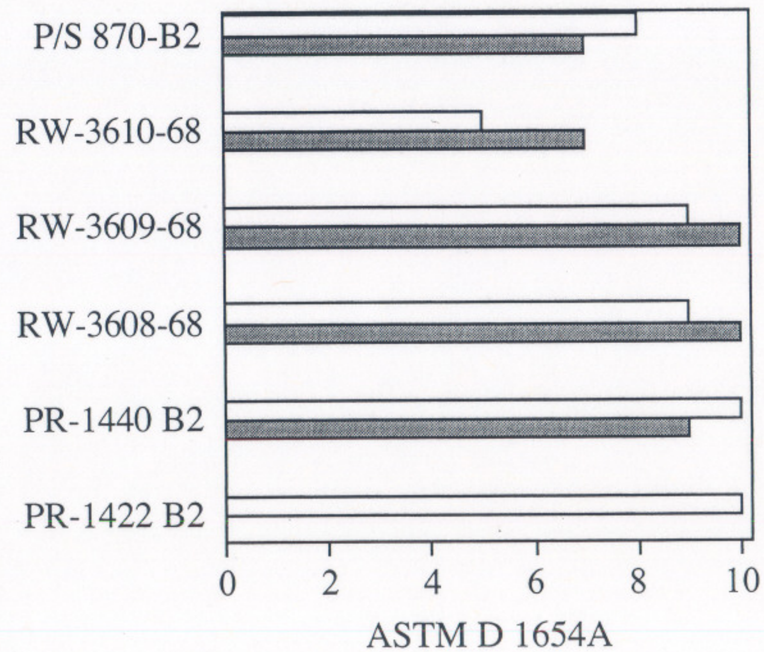


ASTM G 85 A5 (Prohesion) Corrosion

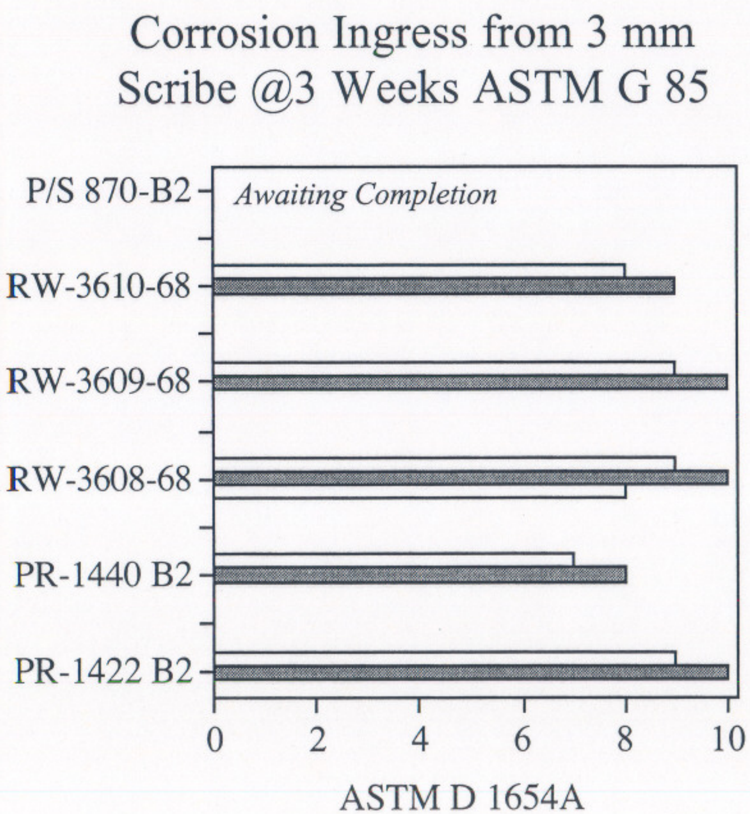
Corrosion Ingress from 3 mm Scribe @2 Weeks ASTM G 85

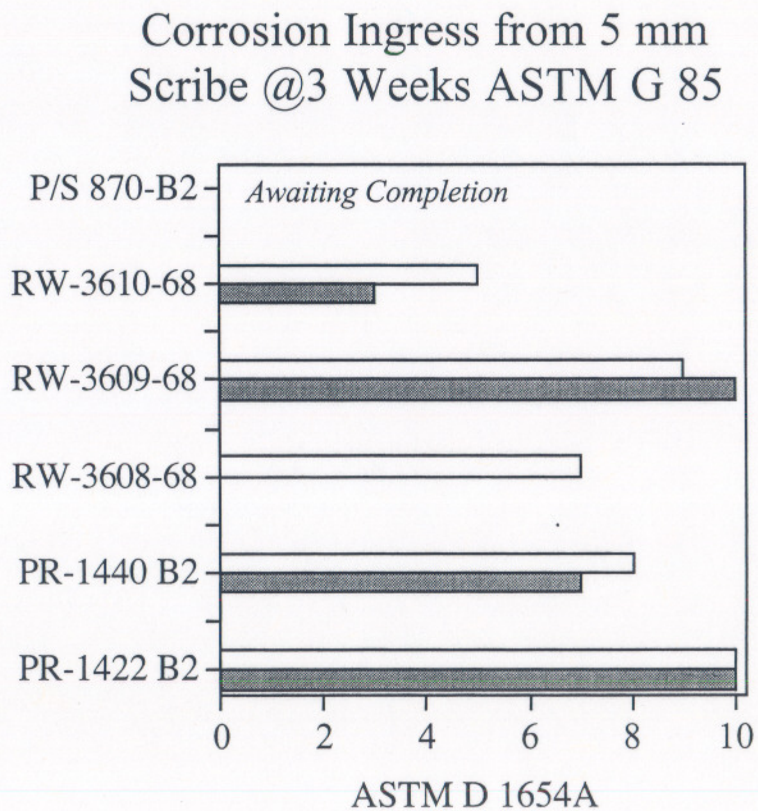


Corrosion Ingress from 5 mm Scribe @2 Weeks ASTM G 85



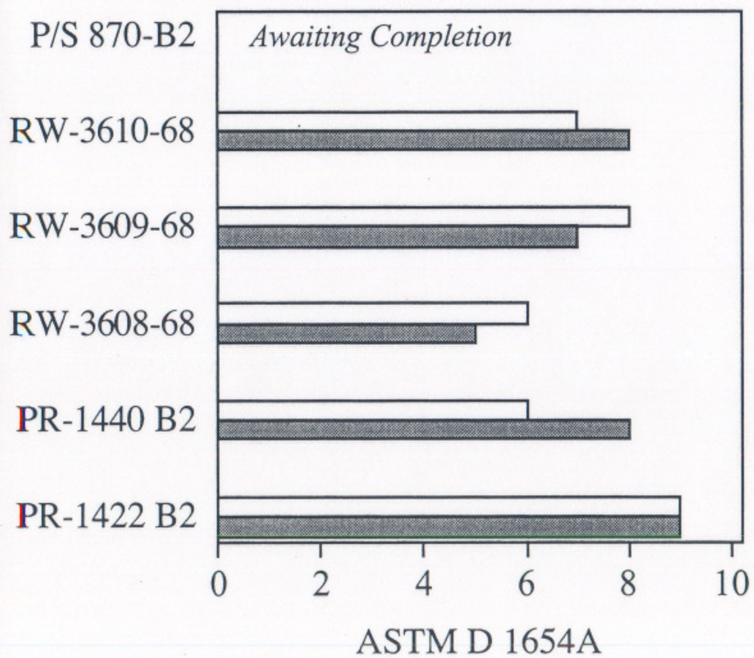
ASTM G 85 A5 (Prohesion) Corrosion



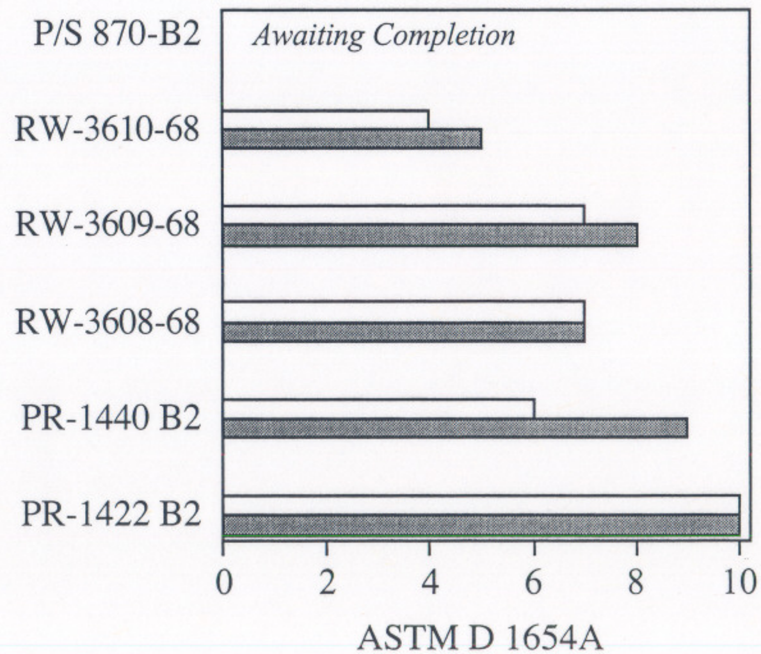


ASTM G 85 A5 (Prohesion) Corrosion

Corrosion Ingress from 3 mm Scribe @4 Weeks ASTM G 85

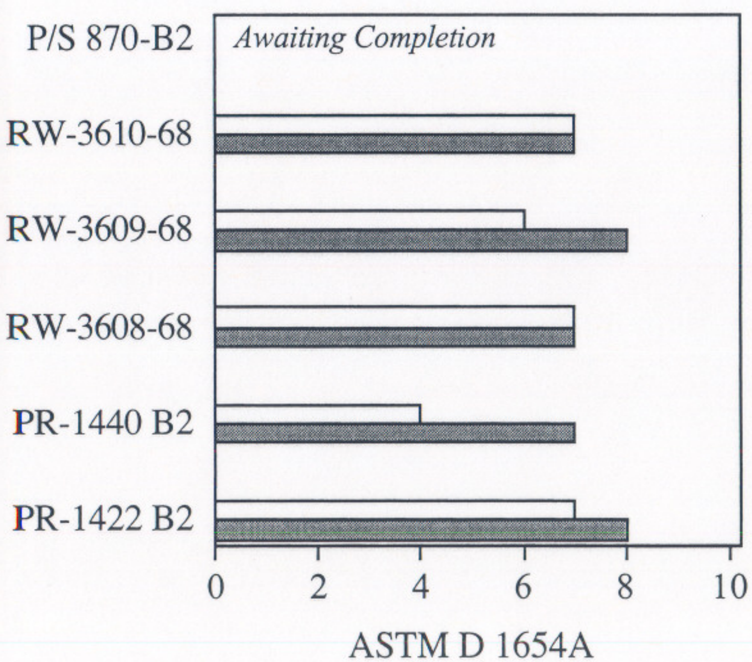


Corrosion Ingress from 5 mm Scribe @4 Weeks ASTM G 85

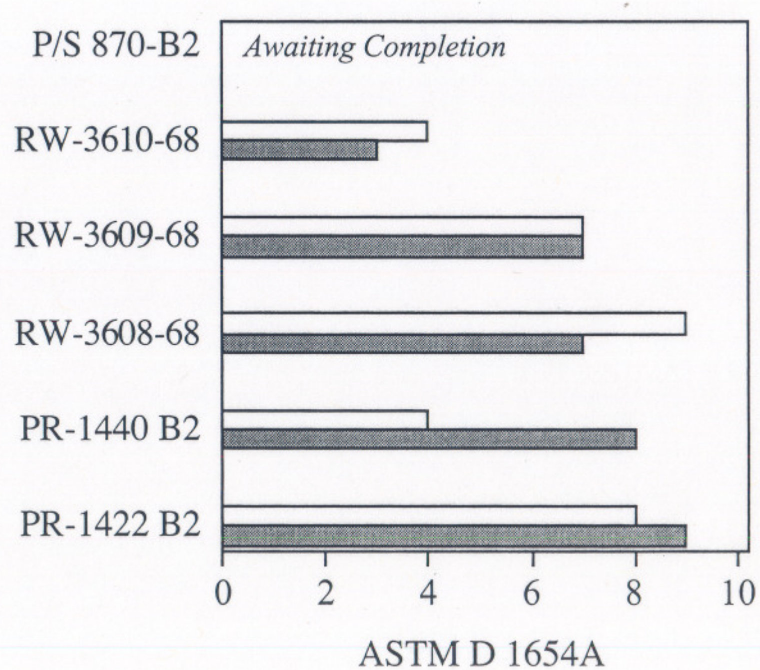


ASTM G 85 A5 (Prohesion) Corrosion

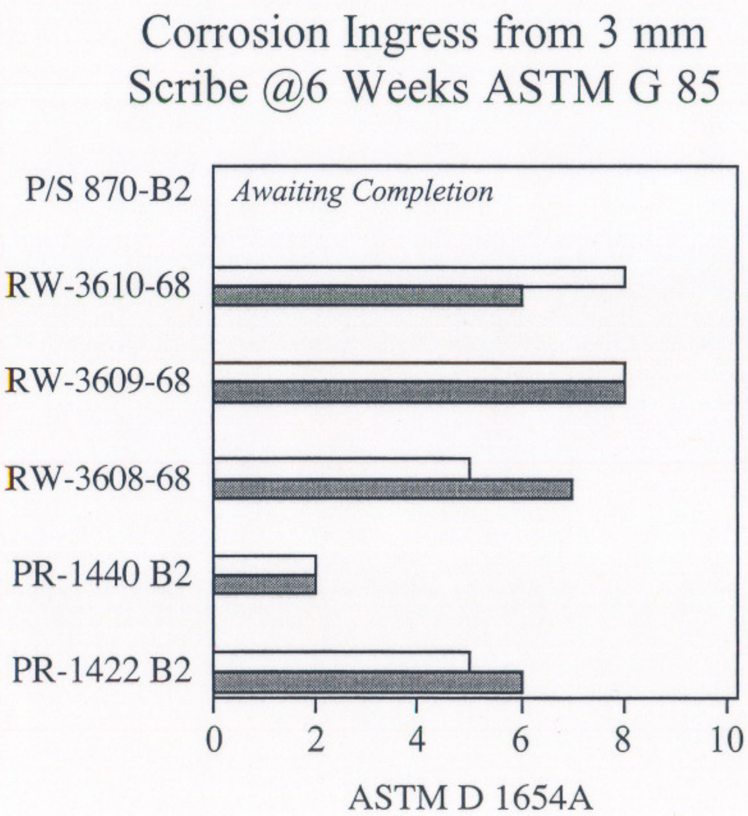
Corrosion Ingress from 3 mm Scribe @5 Weeks ASTM G 85

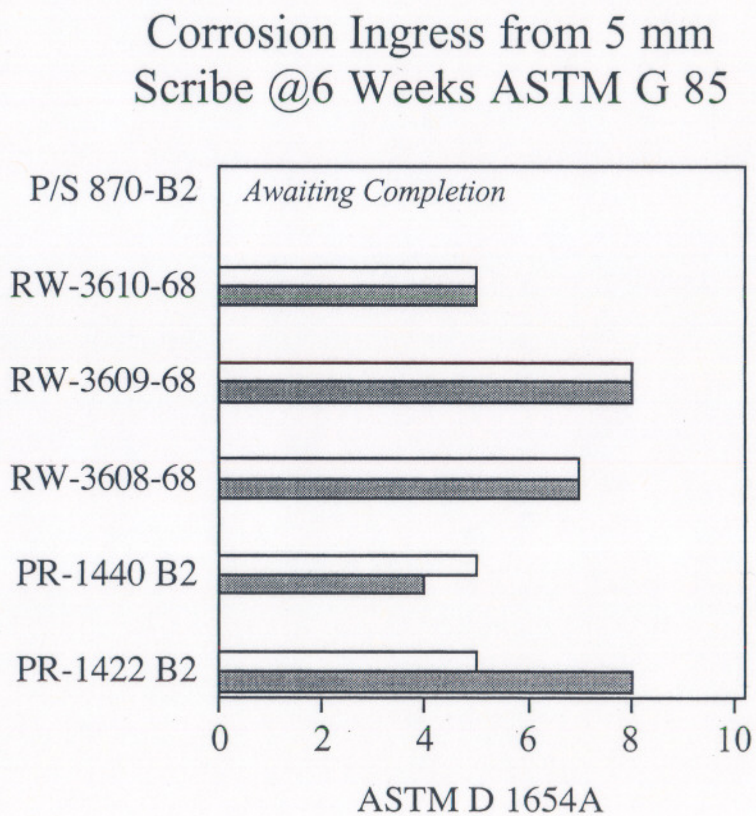


Corrosion Ingress from 5 mm Scribe @5 Weeks ASTM G 85



ASTM G 85 A5 (Prohesion) Corrosion

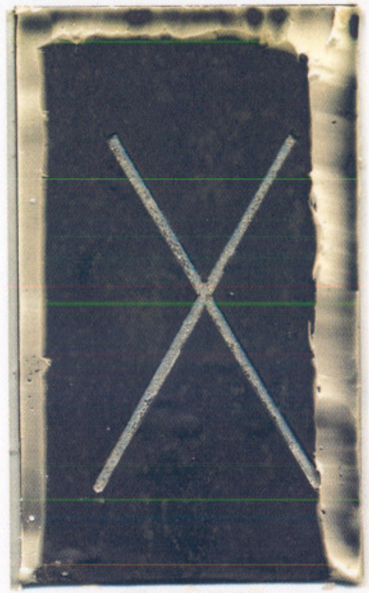




ASTM G 85 A5 (Prohesion) @6 Weeks

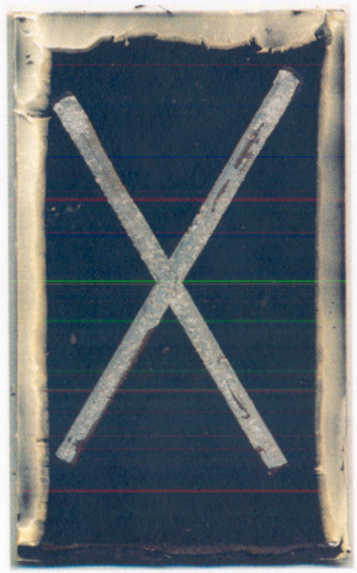
Bare AMS 4045

PR-1422 B2



PR-1440 B2

RW-3608-68

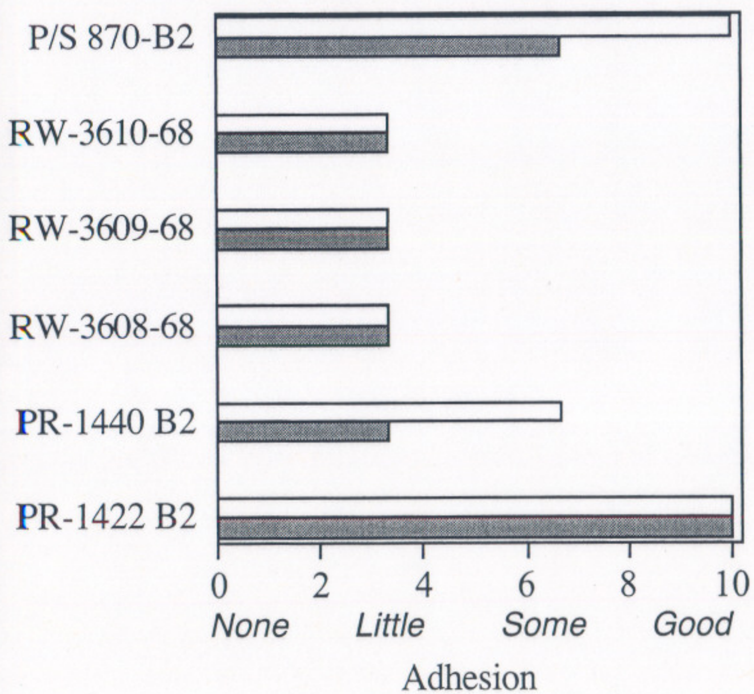


RW-3609-68

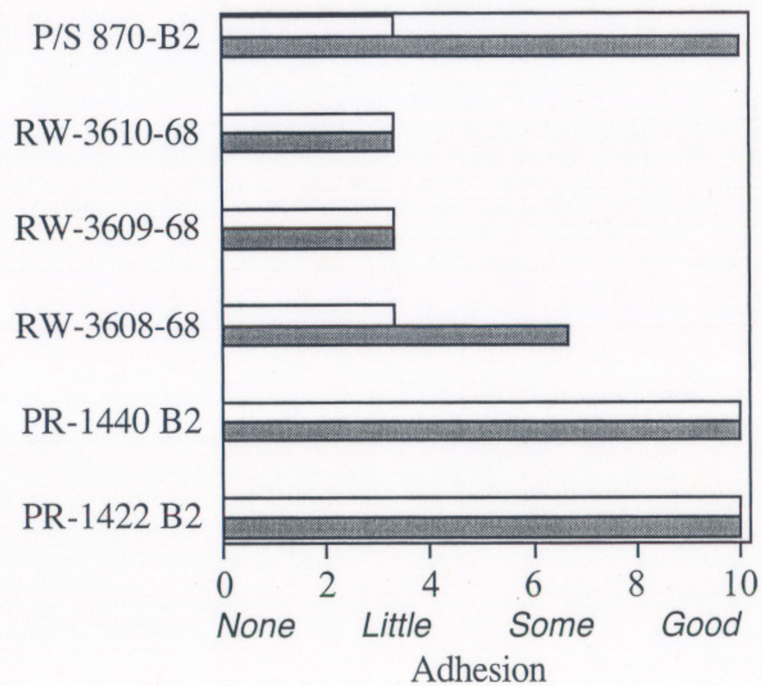
RW 3610-68

ASTM G 85 A5 (Prohesion) Adhesion

3 mm Scribe Adhesion
@1 Week ASTM G 85



5 mm Scribe Adhesion
@1 Week ASTM G 85



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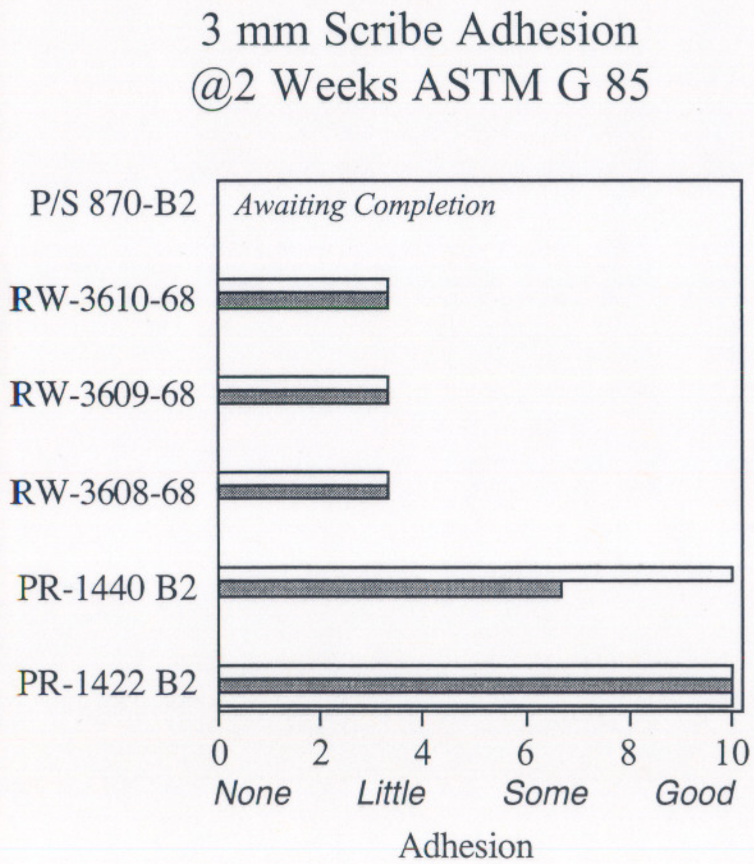

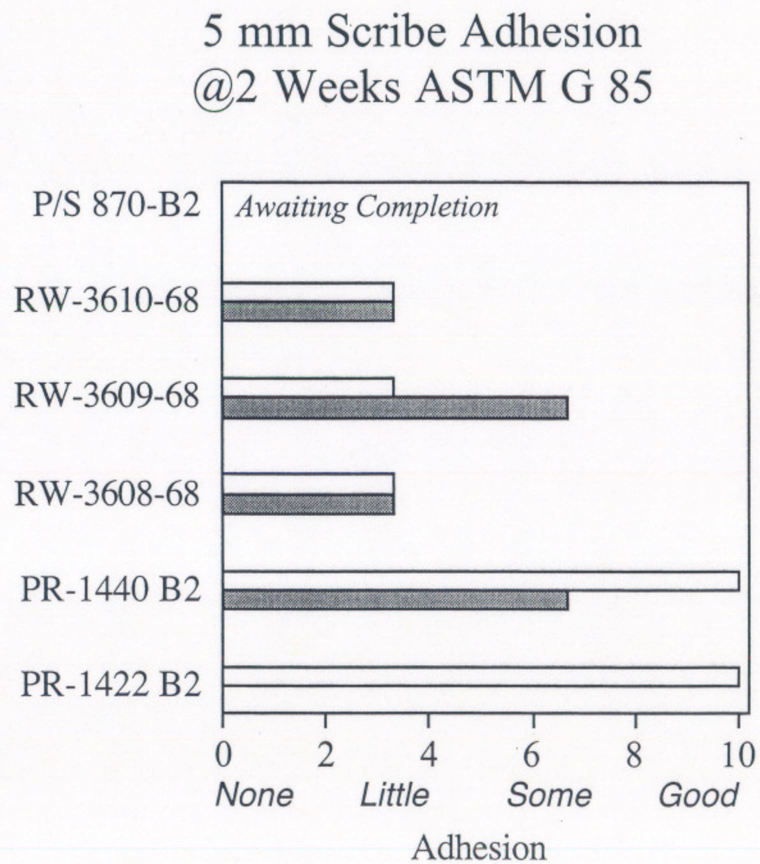

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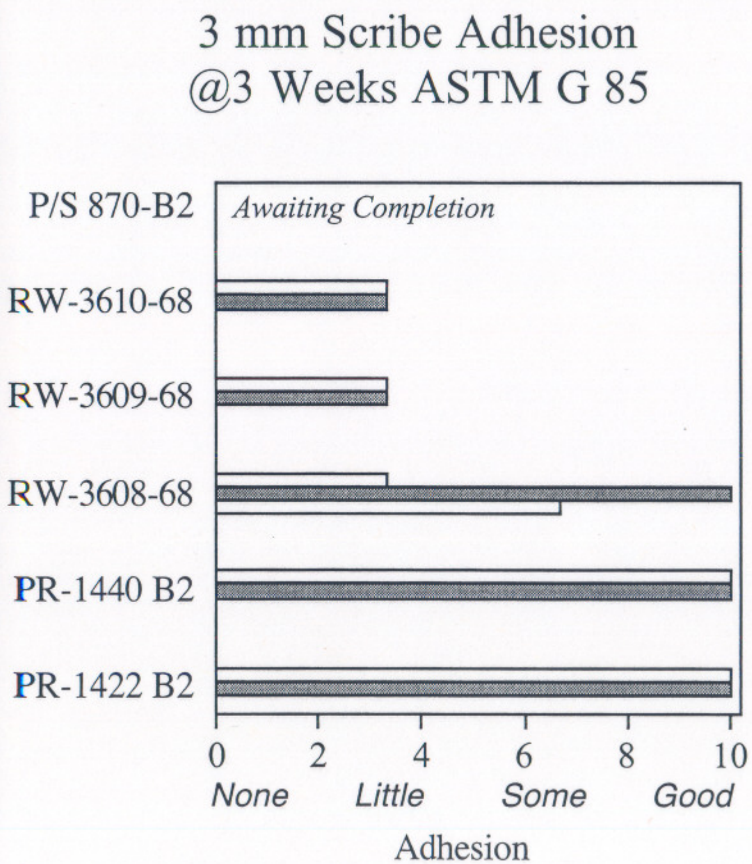

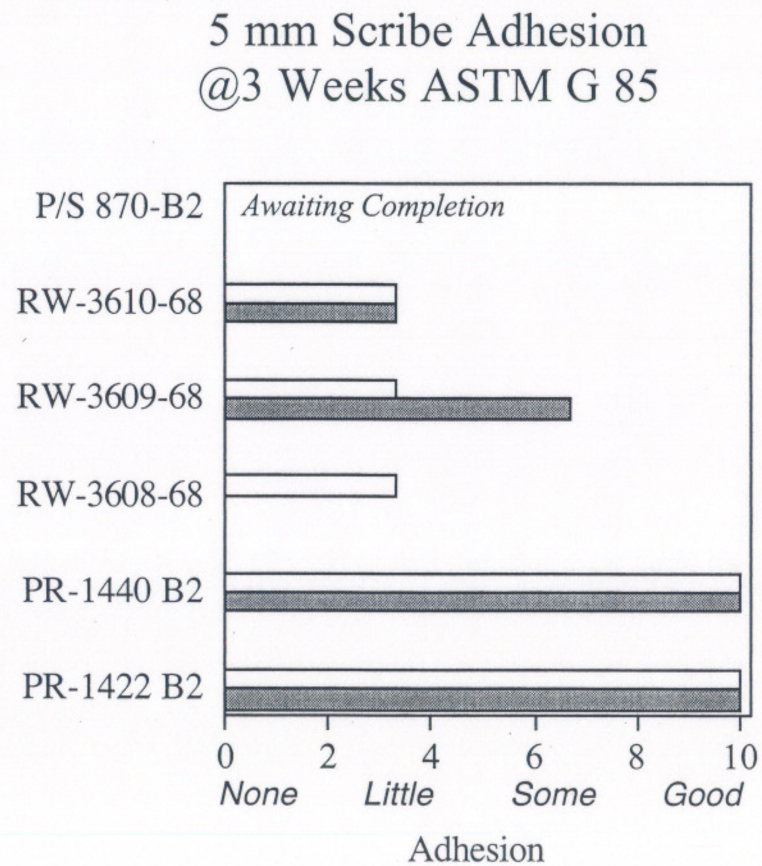

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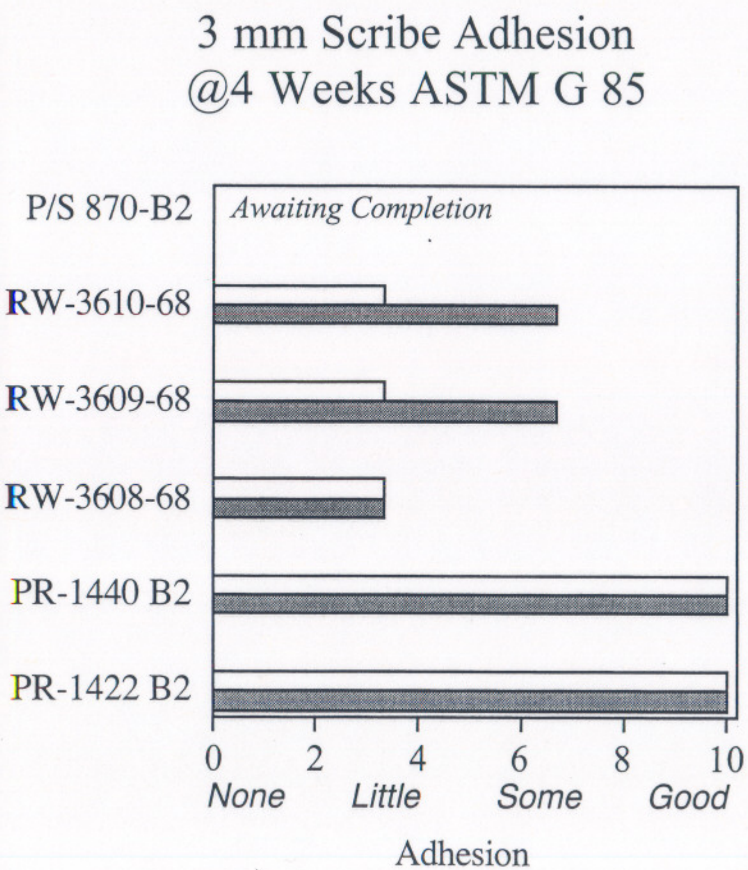

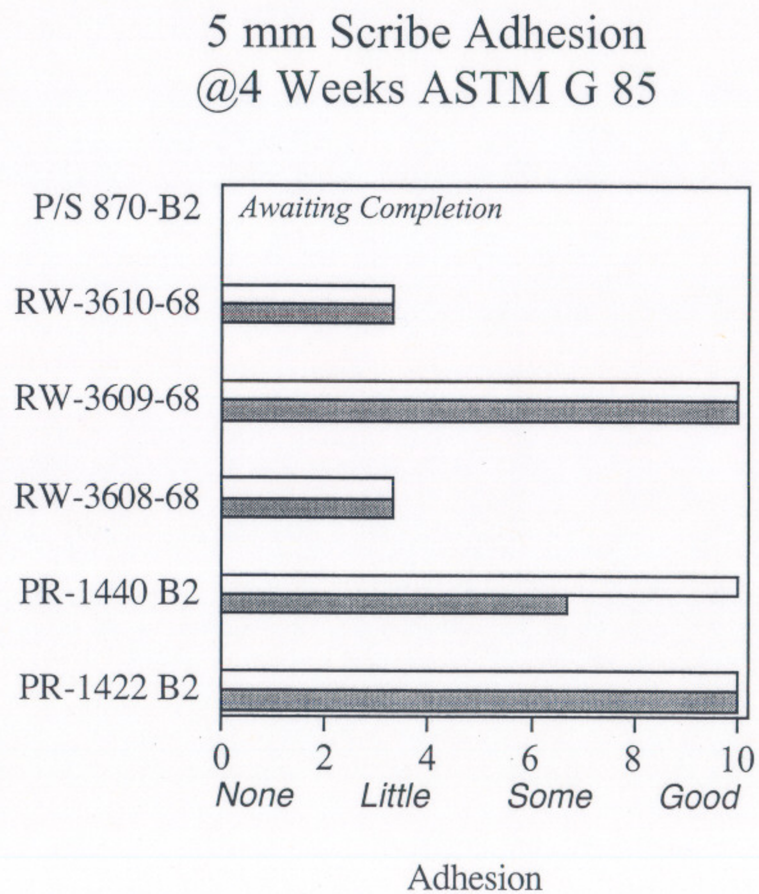

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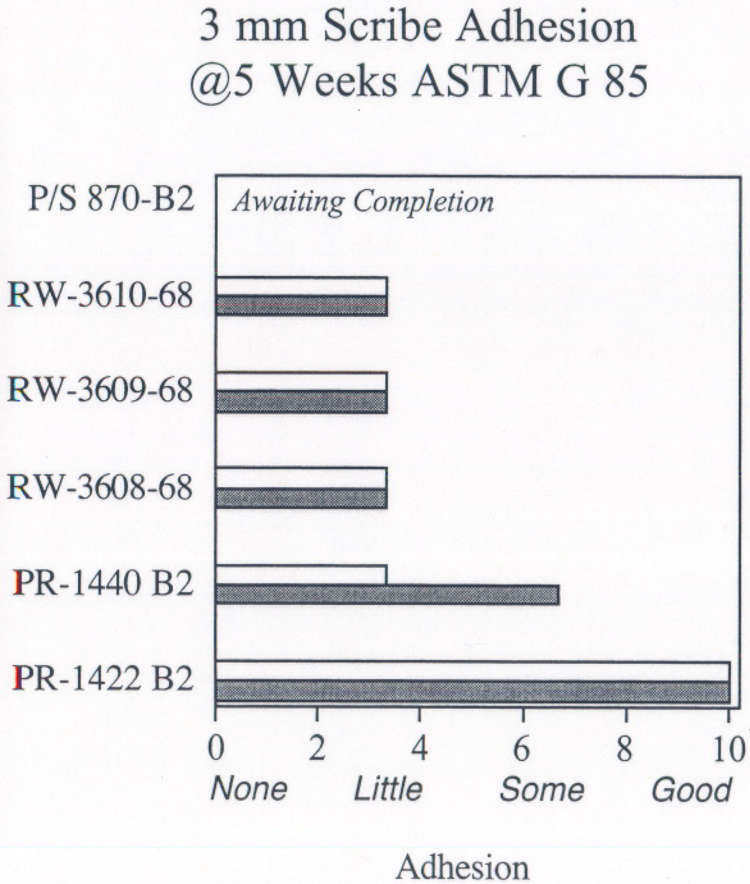

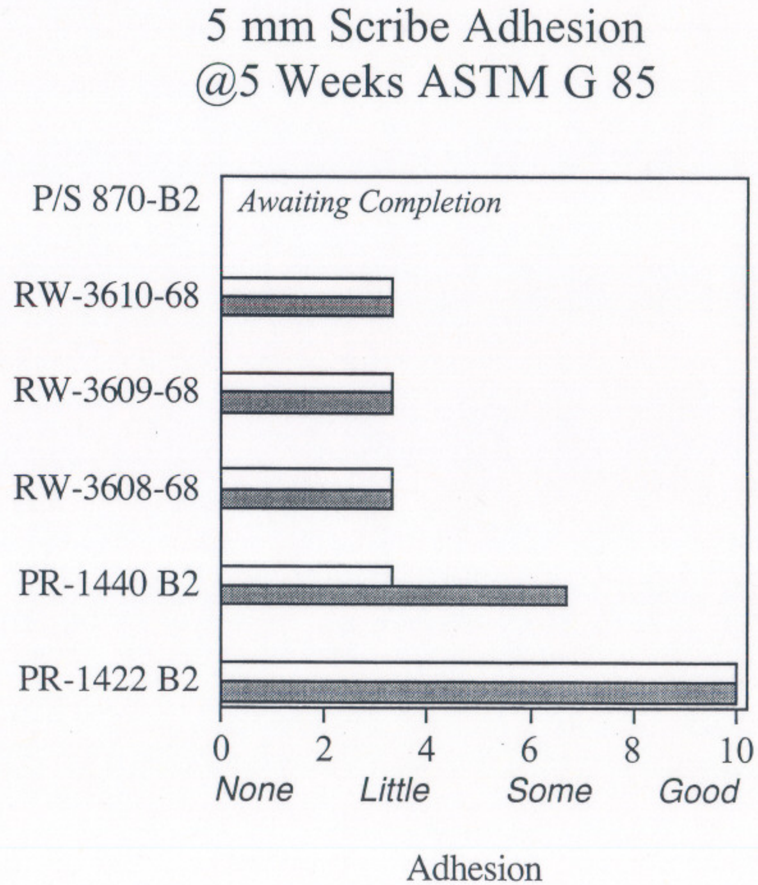

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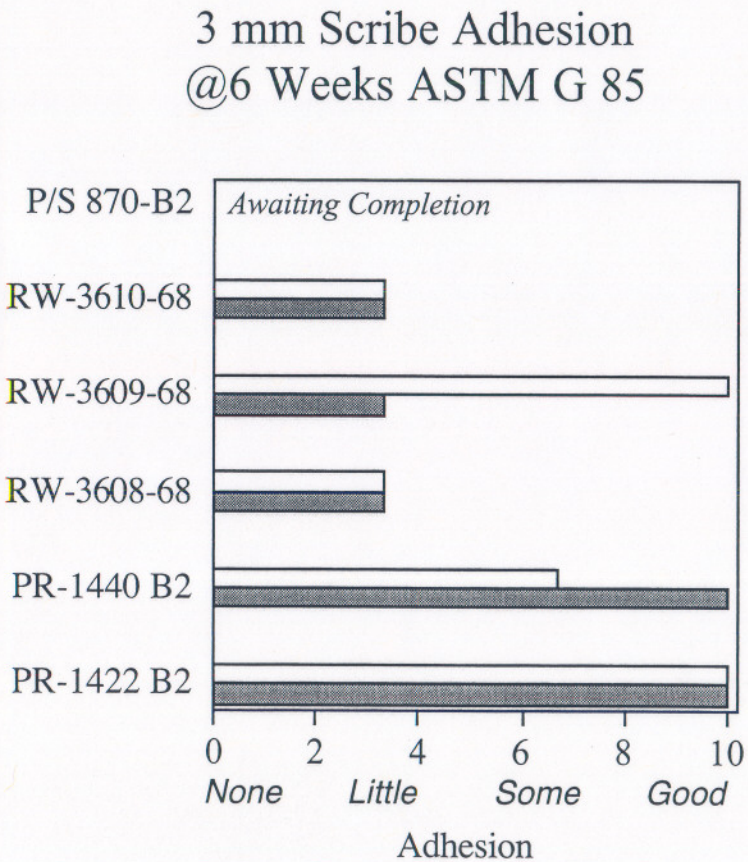

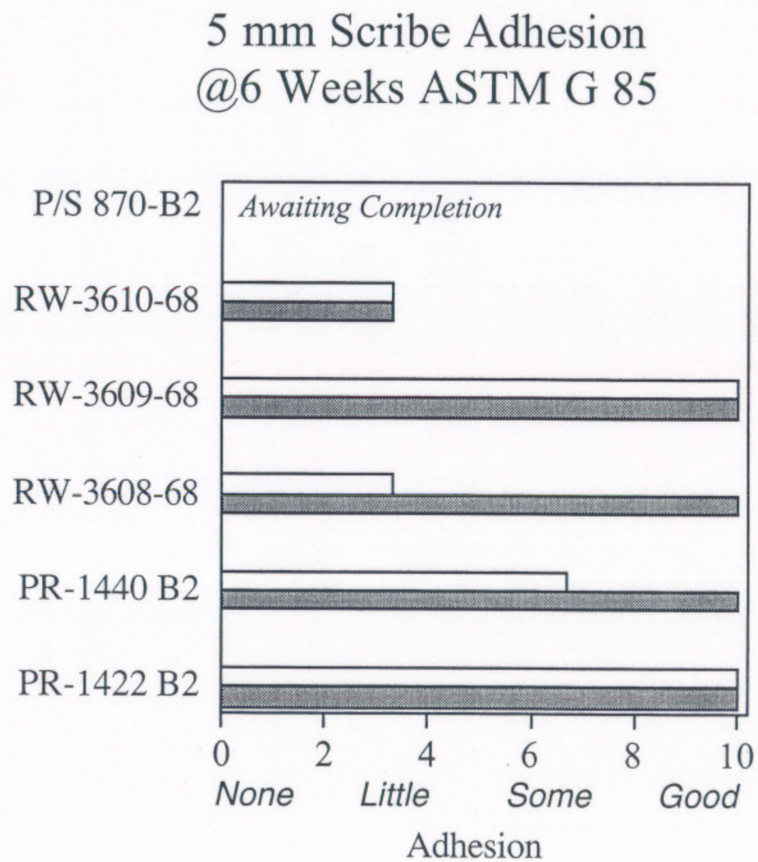

Comments/Conclusions

- Coating thickness varied widely, even among the same coatings.
- The rolling direction of coupons varied.
- Surface finishes varied due to scratches, mill lettering and other imperfections, ultimately impacting adhesion.
- Sealant residuals often remained in scribed regions producing a wide range of results.
- Corrosion away from scribe was only seen on 3 coupons in the entire matrix indicating good impermeability for all of the test sealants.
- Sealant PR 1422-B2 performed best for adhesion in ASTM B 117 and ASTM G 85 A5.
- Sealants 3609-68 and 3610-68 performed best for corrosion resistance followed closely by PR 1422-B2.
- Conclusions are subject to change upon completion of exposure tests for P/S 870 B2.
- Complete XPS results performed by the ARL Polymers Research Branch will follow after the conclusion of exposure tests for P/S 870 B2.

APPENDIX B

TASK 5 CORROSION TESTING BY UDRI AND ARL

REPLACEMENT NON-TOXIC SEALANT FOR STANDARD CHROMATED SEALANTS / SERDP PROJECT NO. 1075

FY01 ANNUAL REPORT

REPLACEMENT NON-TOXIC SEALANTS FOR STANDARD CHROMATED SEALANTS / SERDP Project No. 1075

Alan J. Fletcher
AFRL/MLSA
Materials and Manufacturing Directorate
Air Force Research Laboratory
Systems Support Division
Wright-Patterson AFB, OH 45433-7718

JANUARY 2002

FY 01 Annual Report
Covering Period January 2001 through December 2001

This technical report has been reviewed and is approved for publication.

Michael F. Hitchcock, Chief
MLSA/Materials Integrity Branch
Materials and Manufacturing Directorate
Air Force Research Laboratory
Systems Support Division

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SECTION 1
BACKGROUND AND INTRODUCTION

The preferred corrosion inhibitors for aerospace sealants are chromate-containing compounds. For the chrome to be an effective corrosion inhibitor, the oxidation state must be hexavalent. This form of the chromate is the most hazardous. The primary use of these sealants is to provide a corrosion-resistant barrier between dissimilar metals. A minor quantity can be found in weapons systems that are exposed to non-benign environmental situations. In addition, these sealants contain high VOC solvents (toluene and MEK) that are necessary for proper processing and curing.

Chromated corrosion-inhibiting sealants are typically applied to most faying surfaces in all aircraft that will be exposed to moisture. All military aircraft are required to use this sealant in dry bay areas, wheel wells, cargo bays, radomes, and access panels. Commercial aircraft have the same general uses, but requirements are less stringent. Sometimes these materials are also used to wet-install fasteners, overcoat fasteners, and fillet seal seams.

The sealants industry has been researching and developing new chrome replacement products for several years. One new chromate-free, corrosion-inhibiting sealant has been developed, tested, and transitioned to the field. Replacement for only one class of material has been accomplished so far. There are many more types and classes of materials that need to be developed. Recent advances in polymer chemistry provide a way to develop drop-in replacement materials. This new polymer has some properties that are very beneficial to corrosion-inhibiting sealants such as rapid cure times without reducing work life, a pleasant odor, excellent rheological properties, cure at low temperatures and high solvent resistance. The work included in this effort is directed towards utilizing this new polymer to formulate corrosion-inhibiting sealants for all the types and classes of AMS 3265 sealants.

PRC-DeSoto International, Inc. has developed a new polymer that can be used to formulate corrosion-inhibiting sealant and materials. A subcontract was issued to PRC-DeSoto International, Inc. to develop base polymers, curing agent, corrosion-inhibiting agent, and prototype sealant formulations suitable for a non-chromate corrosion-inhibiting sealant system. PRC-DeSoto International, Inc.'s project consisted of four tasks:

1. Task 1 – Development of Base Compound,
2. Task 2 – Development of Curing Agent,
3. Task 3 – Development of Corrosion-Inhibiting agent, and
4. Task 4 – Development of Prototype Sealant Formulation.

A final report describing the work performed by PRC-DeSoto International, Inc. along with a description of the deliverable product for each task was submitted to UDRI. This report can be found in Appendix A.

PRC-DeSoto International, Inc. submitted one base polymer, DEG-DVE + DMDO (BN: RW-3607-1), and three accelerator packages for evaluation to selected AMS 3265 specification requirements and for the determination of their prohesion properties per ASTM G65, Annex 5. Each of the accelerator packages (BN's RW-3608-68, RW-3609-68, and RW-3610-68) included an optimized curing agent, 60:40 molar blend of Bis A DGE and Bis F Novolac, along with one of three corrosion-inhibitors designated CHNW, CHW, and CNW, respectively.

SECTION 2
PROCEDURE

The Air Force and the University of Dayton Research Institute evaluated three base/accelerator combinations to selected tests from AMS 3265 including:

• Nonvolatile Content	Para. 3.2.2
• Viscosity of Base Compound	Para. 3.2.3
• Hardness	Para. 3.2.4
• Flow	Para. 3.2.6
• Application Time	Para. 3.2.7
• Tack Free Time	Para. 3.2.9
• Standard Cure Time	Para. 3.2.10
• Peel Strength	Para. 3.2.11
MIL-C-5541	
MIL-C-23377 (RT)	
MIL-P-85582	

The corrosion inhibition properties of these three base/accelerator combinations were evaluated by the Air Force/UDRI, Naval Air Warfare Center (NAWC), and the Army Research Lab (ARL). To evaluate the corrosion inhibition properties of the three corrosion resistant sealant combinations both prohesion testing (UDRI & ARL) and salt fog testing (NAWC & ARL) were conducted.

2.1 PROHESION TESTING

The materials were conditioned in a prohesion chamber per ASTM G85, Annex A5 for 6 weeks. In addition, PR-1440 B-2 and PR-1422 B-2, non-corrosion inhibiting sealants qualified to AMS-S- 8802 and PS-870 B-2, a corrosion-inhibiting sealant qualified to MIL-PRF-81733, were conditioned in the same manner. A total of 24 test panels per sealant were placed in the prohesion chamber and the sealant coated test panels were scribed with an "X" down to the metal. One set of sealant-coated panels had a 3-mm wide scribe and the other set had a 5-mm wide scribe. The sealant thickness was ≈ 0.040 inches, and the panel edges were sealed with a one-part flourosilicone sealant. Four samples of each sealant (two 3mm and two 5mm scribed panels) were removed weekly. All sealants were applied to AMS 4045 aluminum substrates for the prohesion testing. AMS 4045 aluminum substrates accompanied the sealant-coated panels for comparison purposes. The corrosion ratings were evaluated per ASTM D 1654-79a (Tables 1 and 2).

2.2 SALT FOG TESTING

The materials were evaluated using salt fog testing according to ASTM B117. As in the prohesion testing, PR-1440 B-2, PR-1422 B-2, and PS-870 B-2 were exposed to the salt fog testing for comparison purposes.

SECTION 3
RESULTS

3.1 APPLICATION AND PERFORMANCE PROPERTIES

The RW-3607-1 base/RW-3608-68 accelerator blend met AMS 3265 specification requirements for 14 day hardness, non-volatile content, application rate at 15 minutes, tack-free time, and std cure rate. The materials initial flow was 0 inches and had 0% cohesive failures on MIL-C-5541, MIL-P-23377, and MIL-P-85582 with AMS 3100 primer. The data are presented in Table 1.

The RW-3607-1 base/RW-3609-68 accelerator blend met AMS 3265 specification requirements for 14 day hardness, non-volatile content, application rate at 15 minutes, tack-free time, and std cure rate, and failed flow. On the MIL-C-5541 substrate the material had 25% cohesive failure after conditioning for 7 days at 140°F (60°C) in AMS 2629 and 90% cohesive failure after the fuel cycle. The remainder of the peel panel substrates exhibited 0% cohesive failures. The data are presented in Table 2.

The RW-3607-1 base/RW-3610-68 accelerator blend met AMS 3265 specification requirements for non-volatile content, application rate at 15 minutes, and tack-free time. The material failed 14 day hardness, flow, and std. cure time. On the MIL-C-5541 substrate the material had 25% cohesive to 90 % cohesive failure on all substrates except MIL-C-5541 after fuel cycle. The data are presented in Table 3.

3.2 PROHESION PROPERTIES

The prohesion data included in the text of this report was generated by UDRI. It should be noted the ARL's test results were almost identical to those presented herein (see Appendix B).

The RW-3607-1/RW-3608-68 had little to some adhesion to the AMS 4045 (7075 bare) aluminum substrate. It protected the 3-mm scribe mark from corrosion on 40% of its surface and prevented excessive creep at the scribe mark for 807 hrs. It protected the 5-mm scribe mark from corrosion on 40% of its surface for 475 hrs. and prevented excessive creep at the scribe mark for 995 hrs. There was no corrosion under the sealant away from the scribe marks. The data are presented in Table 4 with weekly photographs in Figures 1 and 2.

TABLE 1

RW-3607-1 BASE
RW-3608-68 ACCELERATOR

Test	Conditioning	Results	Requirements
14-Day Hardness	Std. Cond.	49 Durometer A	40 Durometer A
Non-Volatile Content	72 hrs @ 158°F(71°C)	98%	92%
Viscosity of Base	Std. Cond.	12,700 pse	9,000 to 18,000 pse
Application Time	30 min @ Std. Cond.	67 gms	15 gms/min
	60 min @ Std. Cond.	0 gms	
Flow	Initial	0 inches	.1 to .75 inches
	50 min.	Could not fill fixture	
Tack-Free Time	Std. Cond.	2.5 hrs	<10 hrs.
Std. Cure Rate	Std. Cond.	35 points @ 7 hrs.	>30 pts @ 30 hrs
Peel Strength			
MIL-C-5541	7 days @ 140°F(60°C) in AMS 2629	21 lbs/2% Coh.	20 lbs/100% Coh
	7 days @ 140°F(60°C) in AMS 2629/ SW	7 lbs/0% Coh 6 lbs/0% Coh	20 lbs/100% Coh 20 lbs/100% Coh
	Fuel Cycle AMS 2629/ SW	5 lbs/0% Coh 4 lbs/0% Coh	20 lbs/100% Coh 20 lbs/100% Coh
MIL-P-23377(RT)	7 Days @ 140°F(60°C)/SW	23 lbs/0% Coh.	20 lbs/100% Coh
MIL-P-85582 w/AMS 3100	7 Days @ 140°F(60°C)/SW	14 lbs/0% Coh	20 lbs/100% Coh

TABLE 2

RW-3607-1 BASE
RW-3609-68 ACCELERATOR

Test	Conditioning	Results	Requirements
14-Day Hardness	Std. Cond.	64 points	40 points
Non-Volatile Content	72 hrs @ 158°F(71°C)	97%	92%
Viscosity of Base	Std. Cond.	12,700 pse	9,000 to 18,000 pse
Application Time	30 min @ Std. Cond.	38 gms	15 gms/min
	60 min @ Std. Cond.	0 gms	
Flow	Initial	0.03 inches	.1 to .75 inches
	50 min.	Could not fill fixture	
Tack-Free Time	Std. Cond.	1.5 hrs	<10 hrs.
Std. Cure Rate	Std. Cond.	58 points @ 5 hrs.	>30 pts @ 30 hrs
Peel Strength			
MIL-C-5541	7 days @ 140°F(60°C) in AMS 2629	16 lbs/25% Coh.	20 lbs/100% Coh
	7 days @ 140°F(60°C) in AMS 2629/ SW	4 lbs/0% Coh 3 lbs/0% Coh	20 lbs/100% Coh 20 lbs/100% Coh
	Fuel Cycle AMS 2629/ SW	18 lbs/98% Coh 19 lbs/90% Coh	20 lbs/100% Coh 20 lbs/100% Coh
MIL-P-23377(RT)	7 Days @ 140°F(60°C)/SW	18 lbs/0% Coh.	20 lbs/100% Coh
MIL-P-85582 w/AMS 3100	7 Days @ 140°F(60°C)/SW	7 lbs/0% Coh	20 lbs/100% Coh

TABLE 3

RW-3607-1 BASE
RW-3610-68 ACCELERATOR

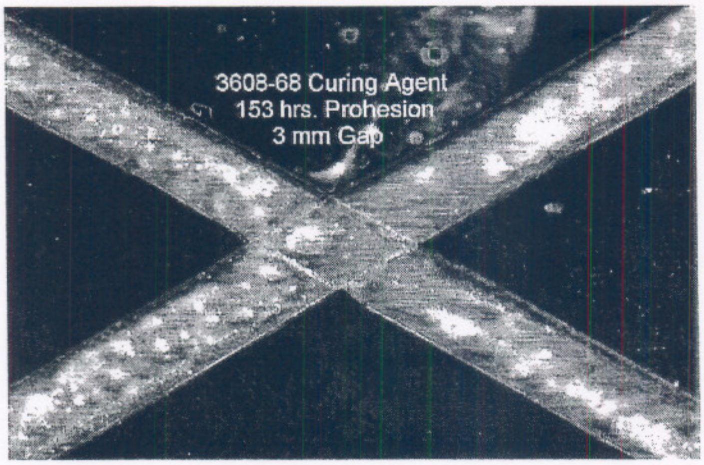
Test	Conditioning	Results	Requirements
14-Day Hardness	Std. Cond.	16 points	40 points
Non-Volatile Content	72 hrs @ 158°F(71°C)	98%	92%
Viscosity of Base	Std. Cond.	12,700 pse	9,000 to 18,000 pse
Application Time	30 min @ Std. Cond.	82 gms	15 gms/min
	60 min @ Std. Cond.	11 gms	
	90 min @ Std. Cond.	0 gms	
Flow	Initial	0 inches	.1 to .75 inches
	50 min.	0 inches	
	90 min.	Could not fill fixture	
Tack-Free Time	Std. Cond.	6 hrs	<10 hrs.
Std. Cure Rate	Std. Cond.	12 points @ 30 hrs.	>30 pts @ 30 hrs
Peel Strength			
MIL-C-5541	7 days @ 140°F(60°C) in AMS 2629	5 lbs/25% Coh.	20 lbs/100% Coh
	7 days @ 140°F(60°C) in AMS 2629/ SW	14 lbs/50% Coh 9 lbs/30% Coh	20 lbs/100% Coh 20 lbs/100% Coh
	Fuel Cycle AMS 2629 SW	6 lbs/0% Coh 3 lbs/0% Coh	20 lbs/100% Coh 20 lbs/100% Coh
MIL-P-23377(RT)	7 Days @ 140°F(60°C)/SW	33 lbs/60% Coh.	20 lbs/100% Coh
MIL-P-85582 w/AMS 3100	7 days @ 140°F(60°C)/SW	27 lbs/90% Coh	20 lbs/100% Coh

TABLE 4

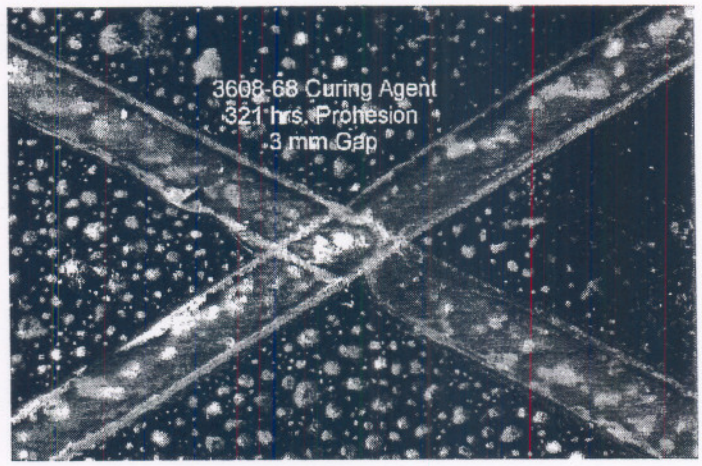
CORROSION RESISTANCE OF RW-3607-1/RW-3608-68

Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
RW-3607-1/	153	3 mm	Little	15	9	10
RW-3608-68	321	3 mm	Some	20	7	10
	475	3 mm	Some	50	7	10
	643	3 mm	Some	55	7	10
	807	3 mm	Some	60	7	10
	995	3 mm	Little	90	0	10
	153	5 mm	Some	20	10	10
	321	5 mm	Some	40	10	10
	475	5 mm	Some	60	9	10
	643	5 mm	Some	70	9	10
	807	5 mm	Some	80	9	10
	995	5 mm	Some	90	7	10

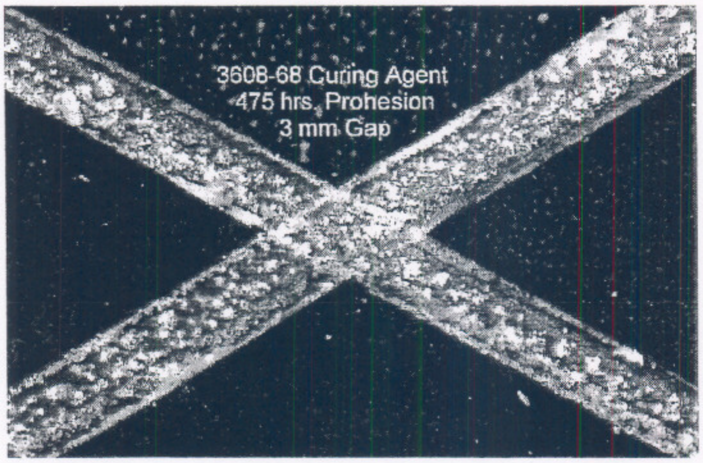
[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe



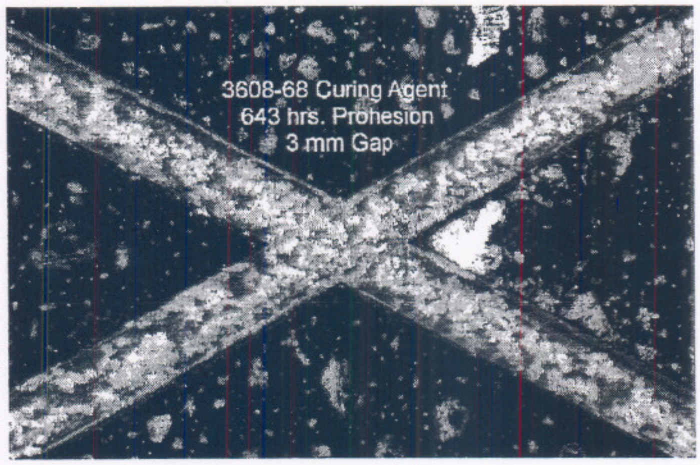
153 hours



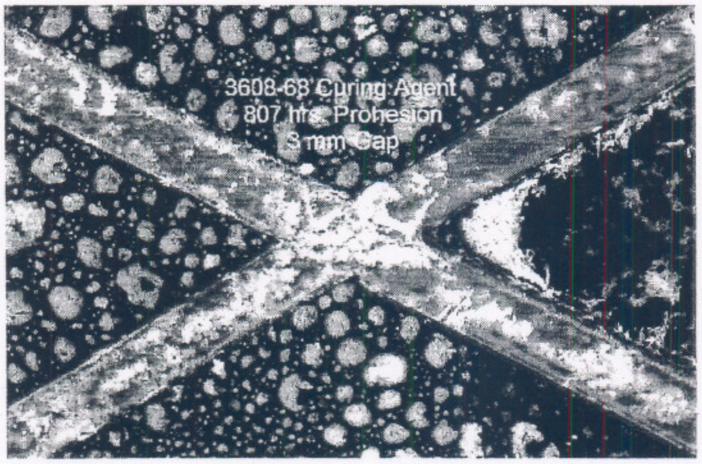
321 hours



475 hours



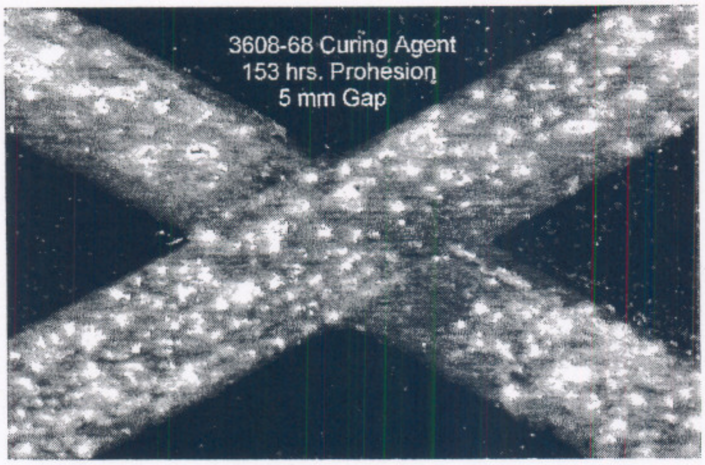
643 hours



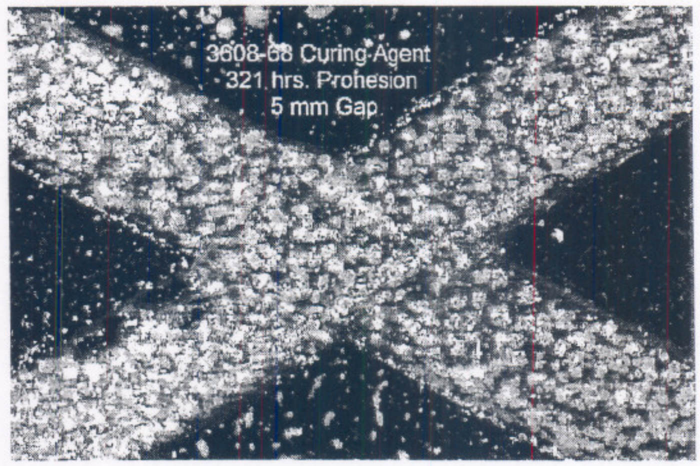
807 hours

995 hours

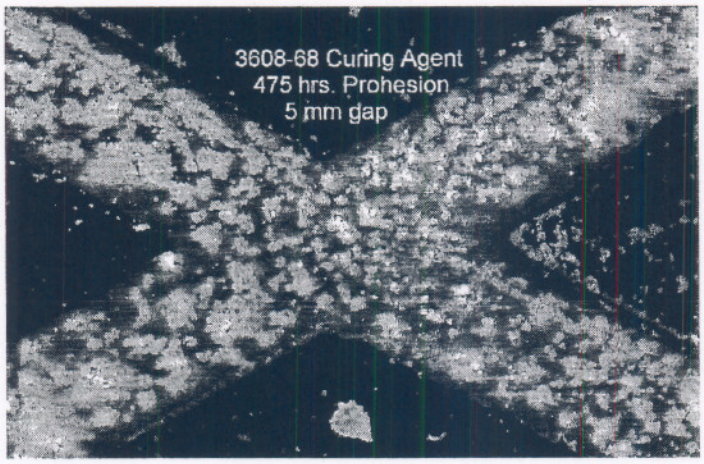
Figure 1. RW-3607-1 / RW-3608-68



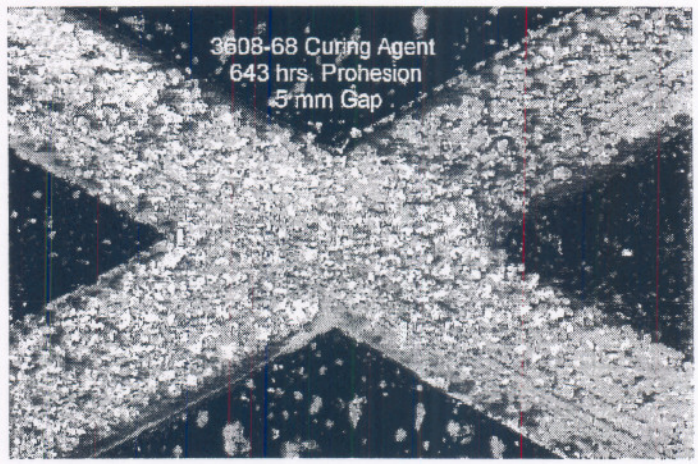
153 hours



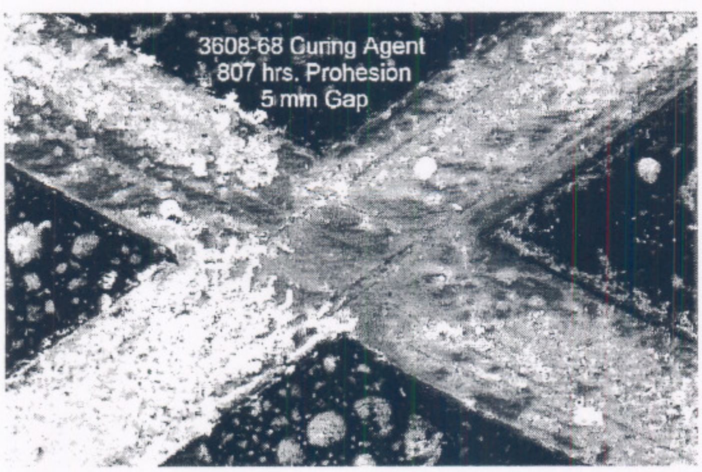
321 hours



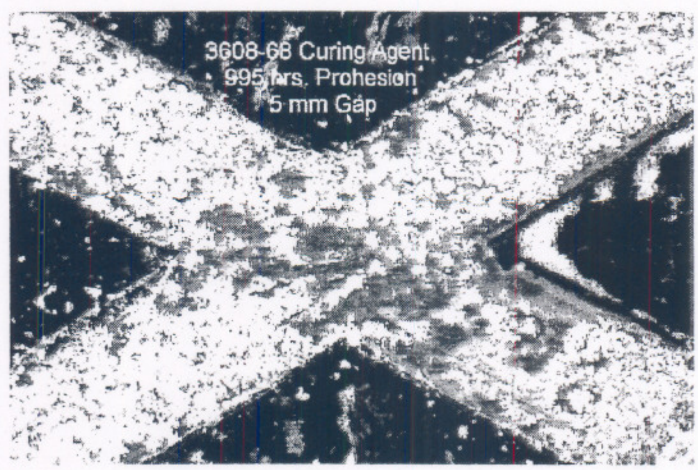
475 hours



643 hours



807 hours



995 hours

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Figure 2. RW-3607-1 / RW-3608-68

The RW-3607-1/RW-3609-68 had some adhesion to the AMS 4045 (7075 bare) aluminum substrate. It protected the 3-mm scribe mark from corrosion on 50% of its surface for 807 hrs and prevented excessive creep at the scribe mark for 995 hrs. It protected the 5-mm scribe mark from corrosion on 40% of its surface for 807 hrs. and prevented excessive creep at the scribe marks for 995 hrs. There was no corrosion under the sealant away from the scribe marks. The data are presented in Table 5 with weekly photographs in Figures 3 and 4.

The RW-3607-1/RW-3610-68 had little to some adhesion to the AMS 4045 (7075 bare) aluminum substrate. It protected the 3-mm scribe mark from corrosion on 50% of its surface for 995 hrs and prevented excessive creep at the scribe mark for 807 hrs. It protected the 5-mm scribe mark from corrosion on 40% of its surface for 995 hrs. and prevented excessive creep at the scribe marks for 995 hrs. There was no corrosion under the sealant away from the scribe marks. The data are presented in Table 6 with weekly photographs in Figures 5 and 6.

PR-1422 B-2, a Type 1 dichromate cured polysulfide sealant qualified to AMS-S-8802, did not prevent total corrosion in the 3-mm and 5-mm scribe after 475 hrs. The material had very good adhesion to the AMS 4045 aluminum but started blistering after 807 hrs. The PR-1422 B-2 had excellent corrosion creep resistance until 995 hrs and good corrosion resistance under the sealant. The data are presented in Table 7 with weekly photographs in Figures 7 and 8.

The PR-1440 B-2, a Type II manganese cured polysulfide sealant qualified to AMS-S-8802, did not prevent complete corrosion in the scribe after 643 hrs. The material had good adhesion to the AMS 4045 substrate. The material prevented excessive creep of the corrosion and good corrosion resistance under the sealant. The data are presented in Table 8 with weekly photographs in Figures 9 and 10.

PS-870 B-2, a corrosion resistant sealant qualified to MIL-PRF-81733, did not prevent complete corrosion in the 3-mm scribe after 504 hrs. and the 5-mm scribe after 672 hrs. The material allowed excessive creep after 672 hrs. on the 3-mm scribe because it blistered. This blistering did not occur on the 5-mm scribe panel. The PS-870 B-2 had good corrosion resistance under the sealant. The data are presented in Table 9 with weekly photographs in Figures 11 and 12.

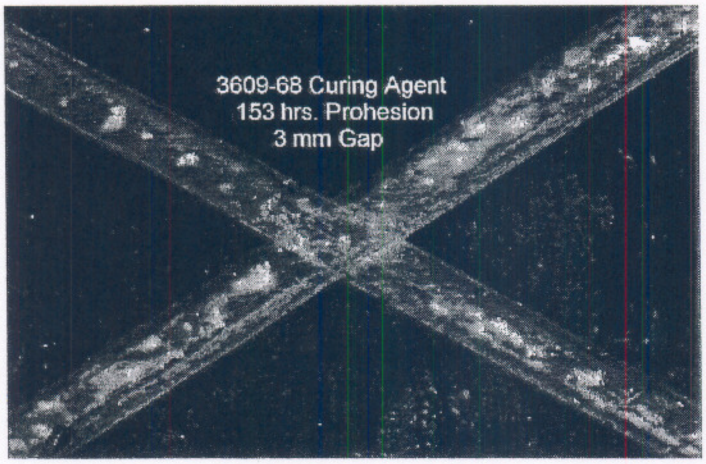
TABLE 5

CORROSION RESISTANCE of RW-3607-1/RW-3609-68

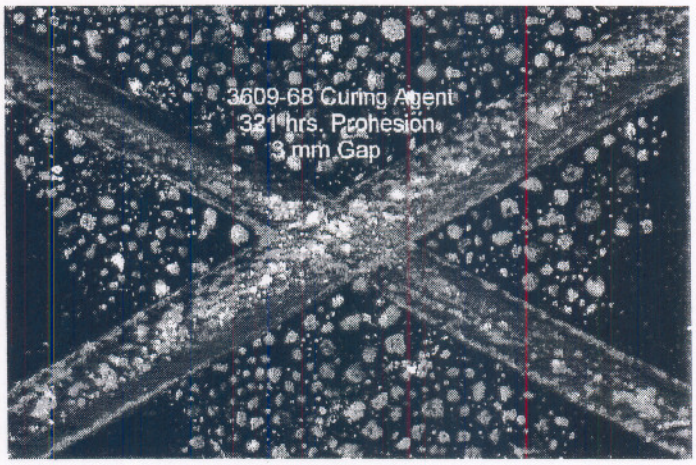
Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
RW-3607-1/	153	3 mm	Little	15	10	10
RW-3609-68	321	3 mm	Some	15	8	10
	475	3 mm	Some	30	8	10
	643	3 mm	Some	40	8	10
	807	3 mm	Some	50	8	10
	995	3 mm	Some	90	8	10
	153	5 mm	Some	20	9	10
	321	5 mm	Some	30	10	10
	475	5 mm	Some	50	10	10
	643	5 mm	Some	60	10	10
	807	5 mm	Some	60	8	10
	995	5 mm	Some	90	8	10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion

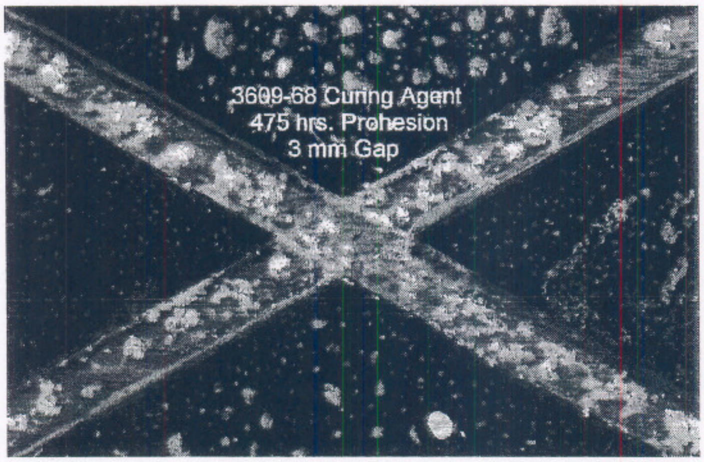
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe



153 hours

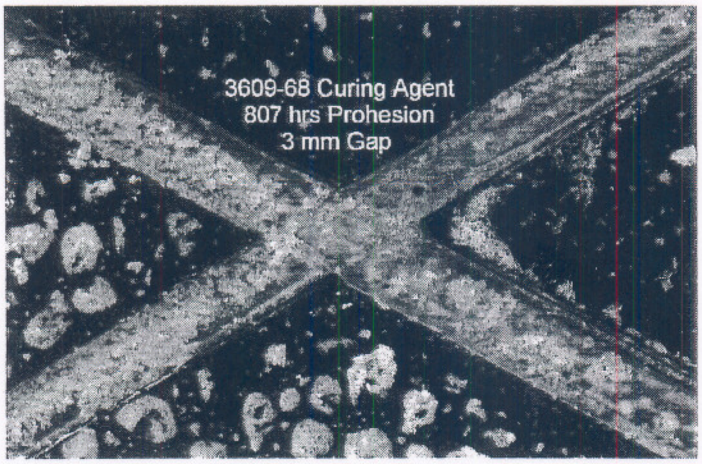


321 hours



475 hours

643 hours



807 hours

995 hours

Figure 3. RW-3607-1 / RW-3609-68

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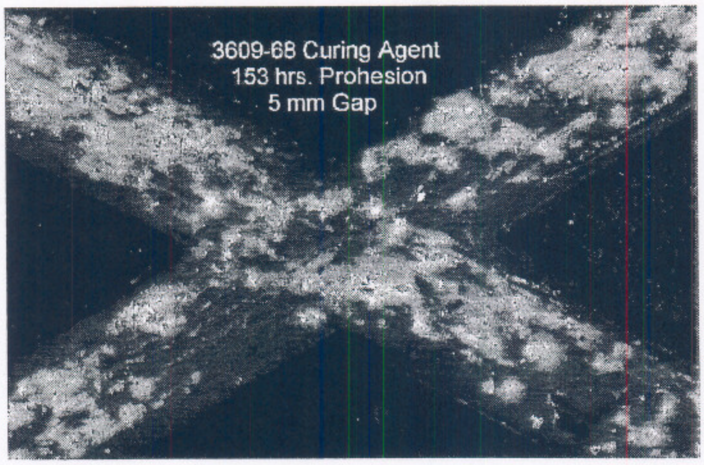

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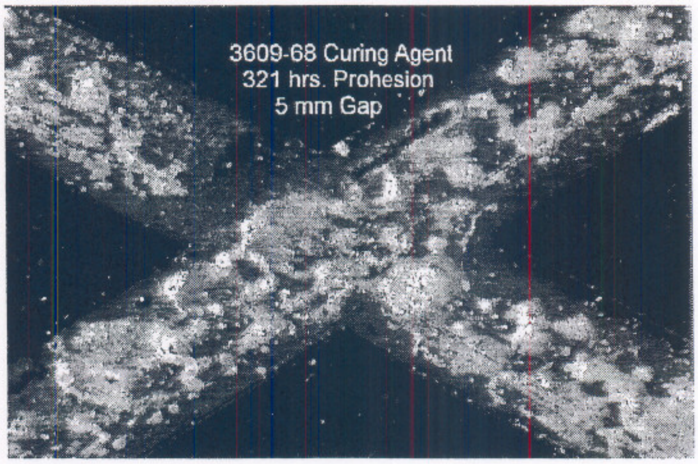

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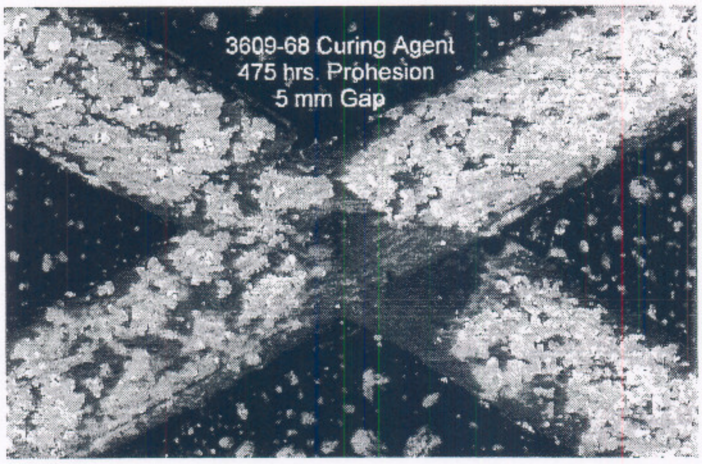

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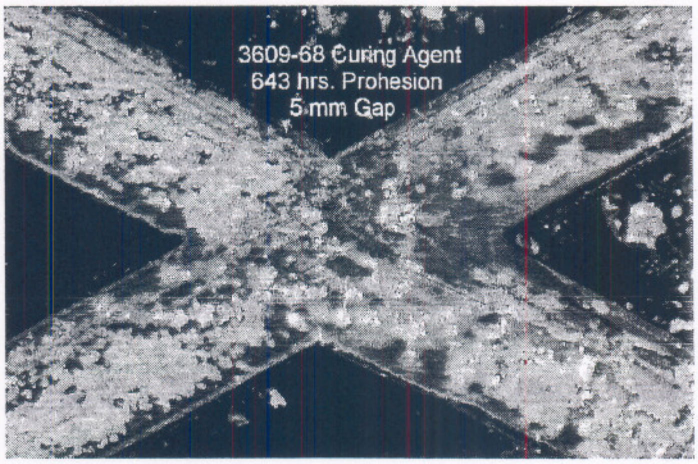
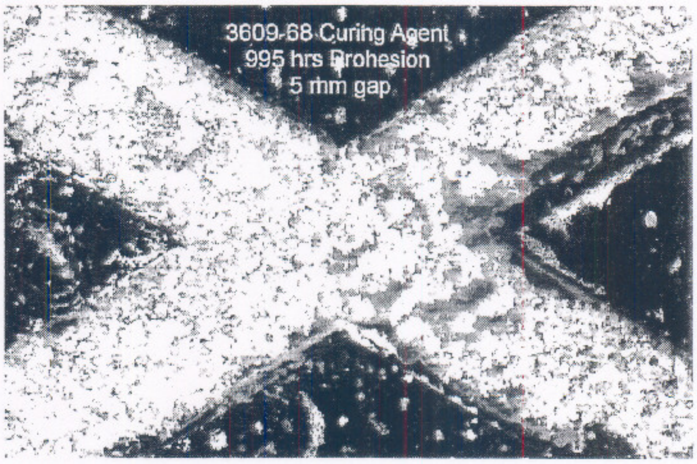


643 hours

807 hours



995 hours

Figure 4. RW-3607-1 / RW-3609-68

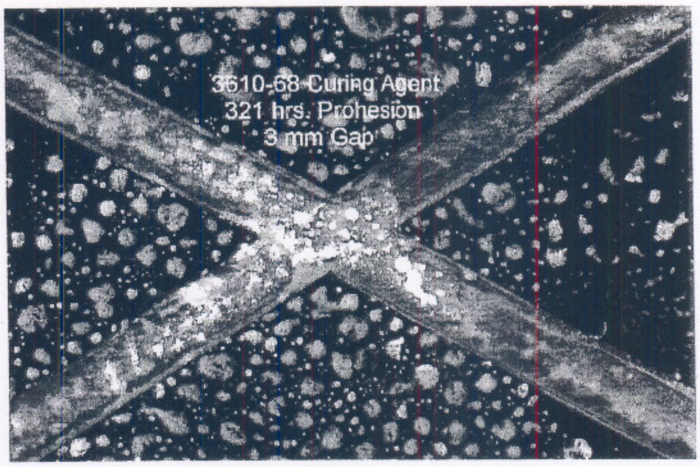
TABLE 6

CORROSION RESISTANCE OF RW-3607-1/RW-3610-68

Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
RW-3607-1/	153	3 mm	Some	15	10	10
RW-3610-68	321	3 mm	Little	20	7	10
	475	3 mm	Some	25	9	10
	643	3 mm	Some	30	8	10
	807	3 mm	Some	40	8	10
	995	3 mm	Little	50	0	10
	153	5 mm	Some	30	9	10
	321	5 mm	Little	40	9	10
	475	5 mm	Little	50	9	10
	643	5 mm	Some	60	9	10
	807	5 mm	Some	50	9	10
	995	5 mm	Some	60	9	10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe

153 hours

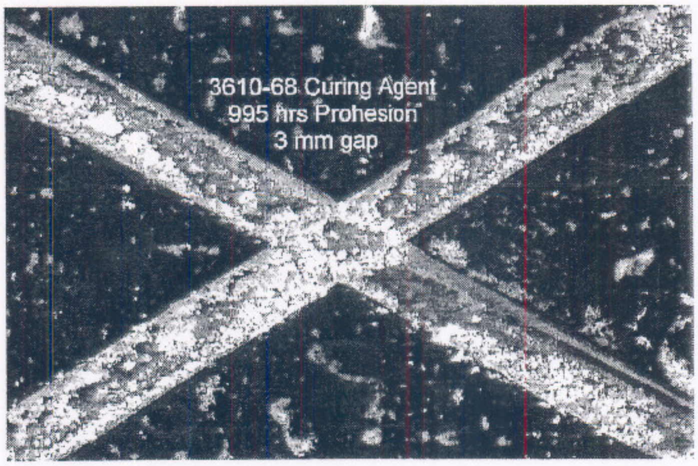


321 hours

475 hours

643 hours

807 hours



995 hours

Figure 5. RW-3607-1 / RW-3610-68

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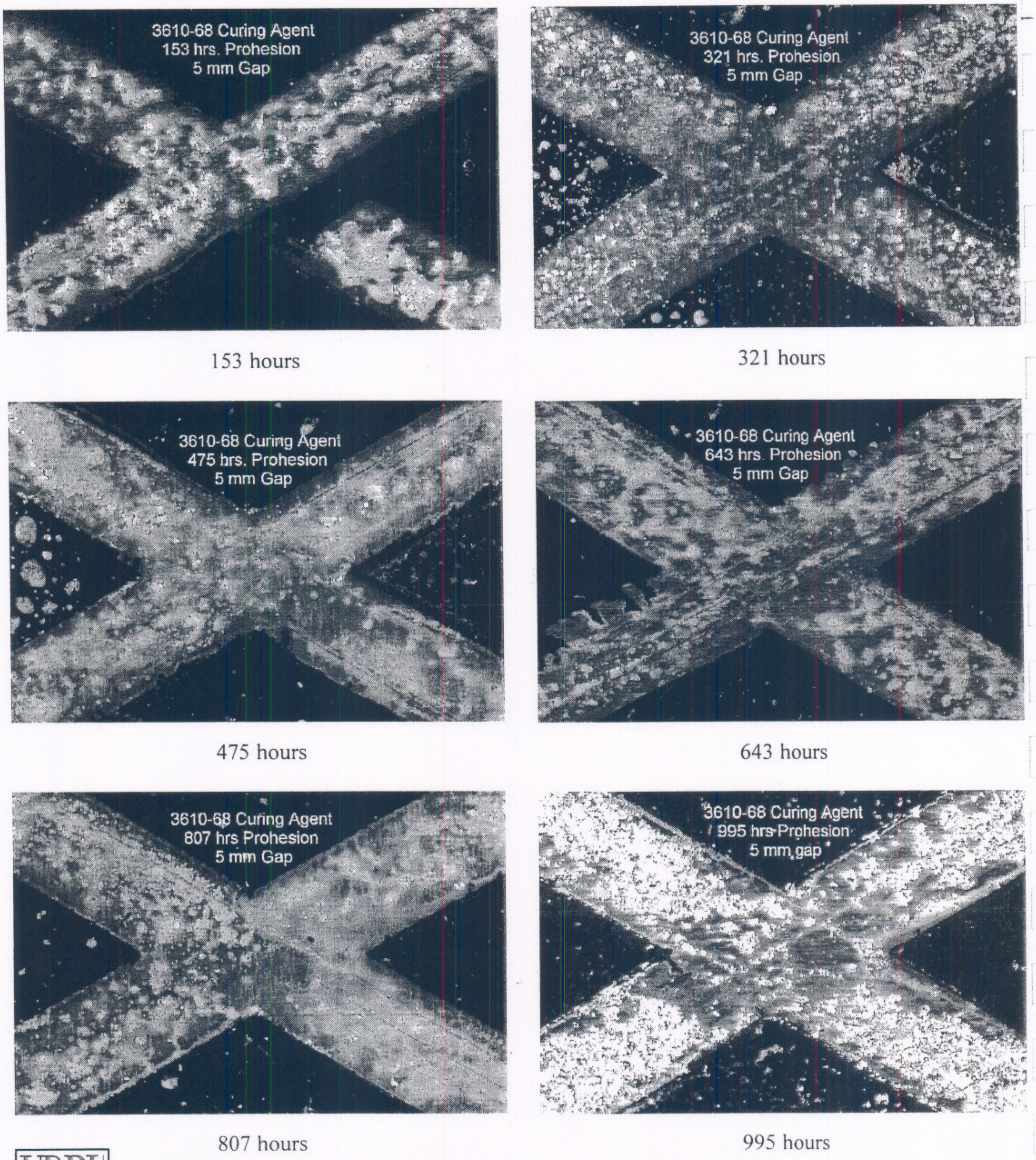


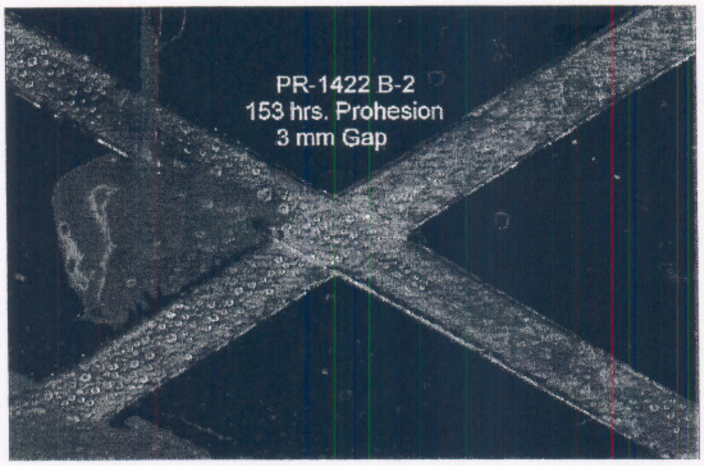
Figure 6. RW-3607-1 / RW-3610-68

TABLE 7

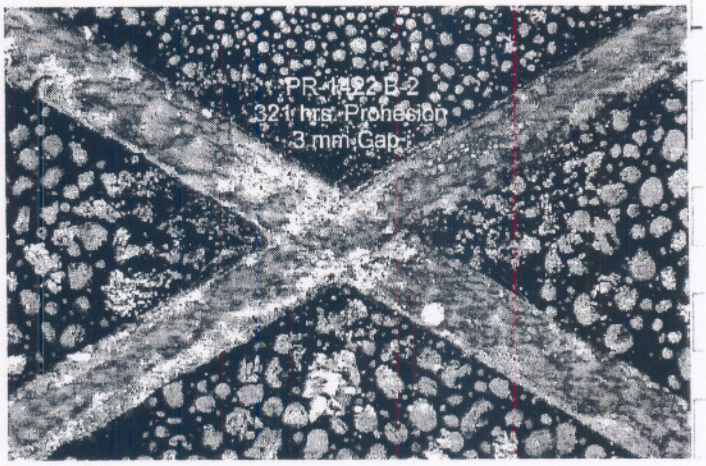
CORROSION RESISTANCE OF PR-1422 B-2

Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
PR-1422 B-2	153	3 mm	Good	10	10	10
	321	3 mm	Good	50	10	10
	475	3 mm	Good	60	10	10
	643	3 mm	Good	90	10	10
	807	3 mm	Blistered	95	10	9
	995	3 mm	Blistered	100	0	10
	153	5 mm	Good	5	10	10
	321	5 mm	Good	50	10	10
	475	5 mm	Good	70	10	10
	643	5 mm	Good	80	10	10
	807	5 mm	Blistered	95	10	9
	995	5 mm	Blistered	100	0	10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe



153 hours



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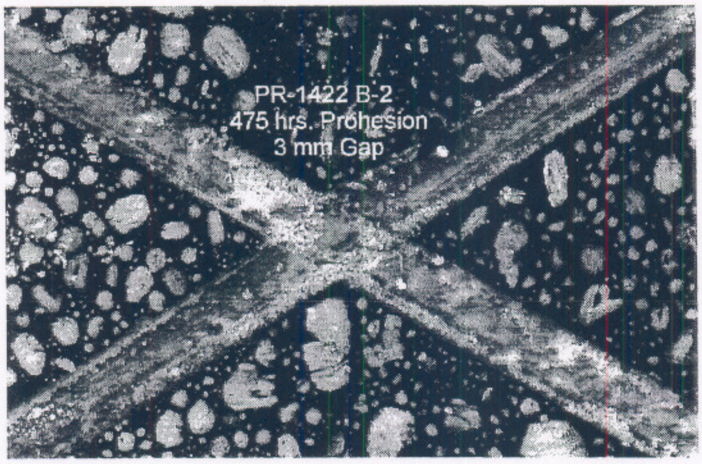
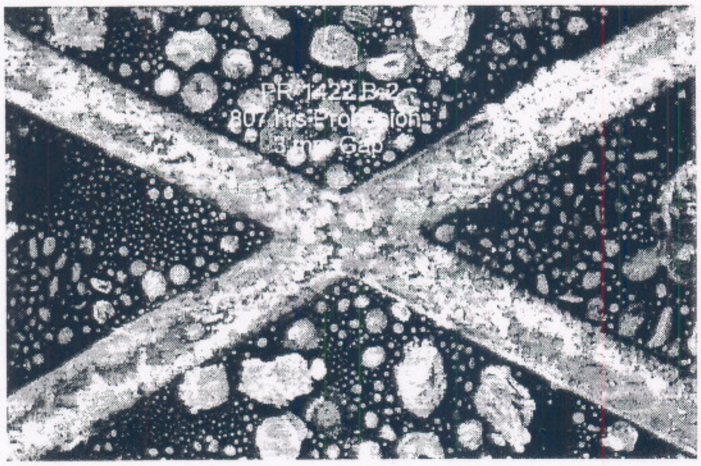


475 hours

643 hours



807 hours

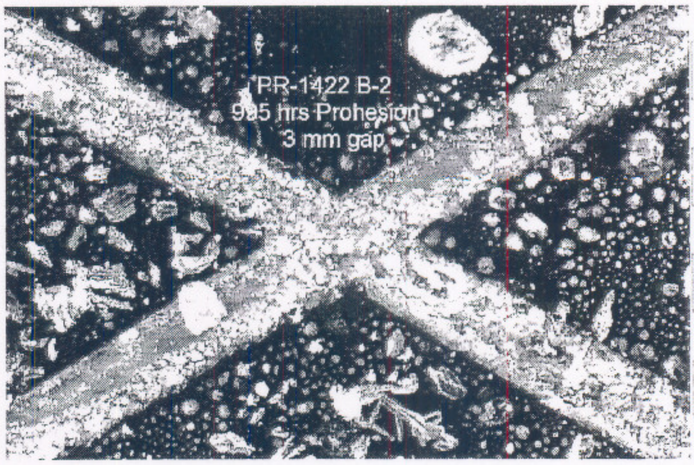


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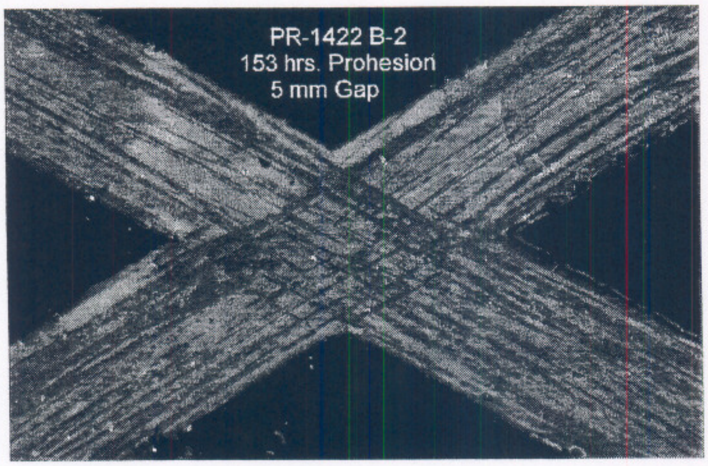
Figure 7. PR-1422 B-2



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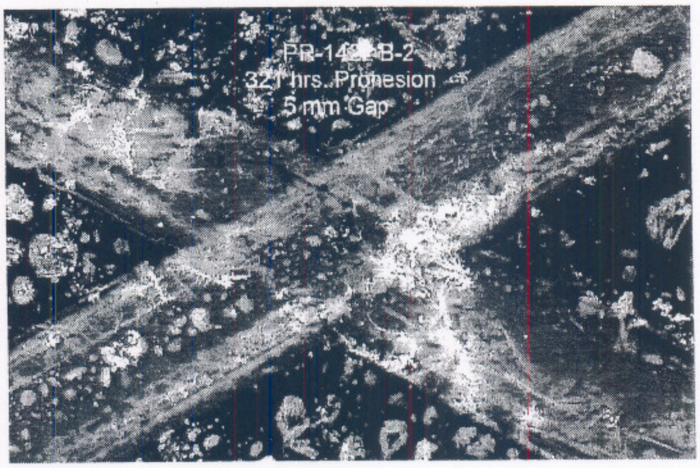

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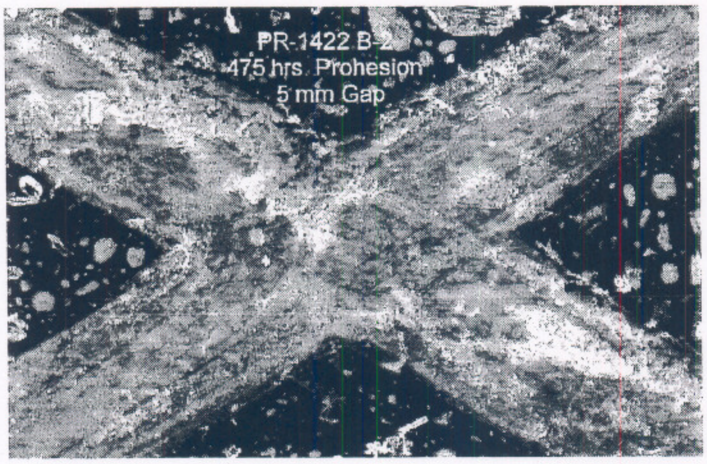

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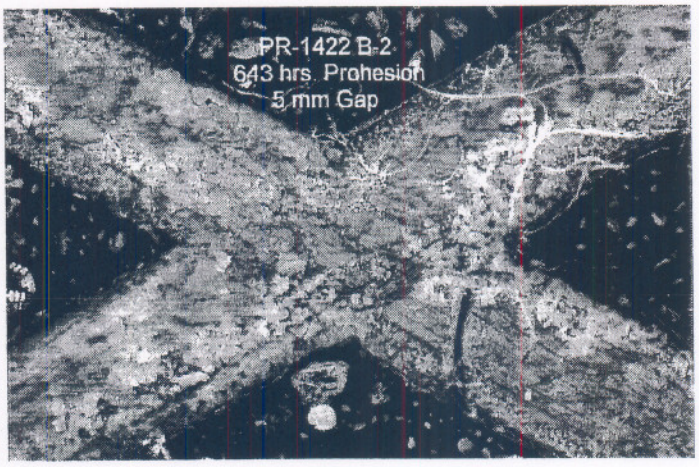

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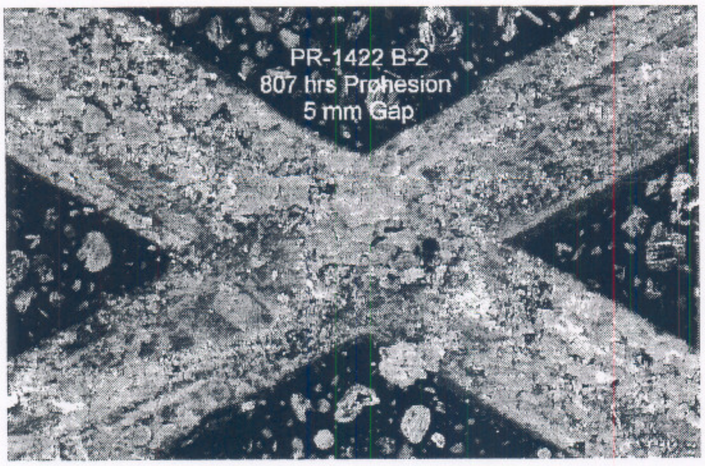

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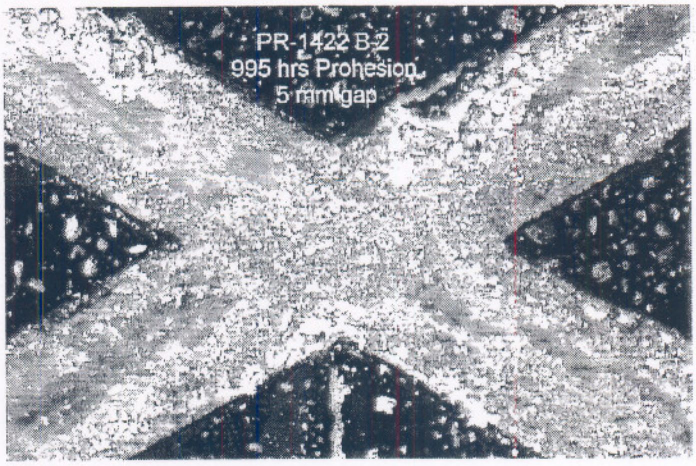


995 hours

Figure 8. PR-1422 B-2

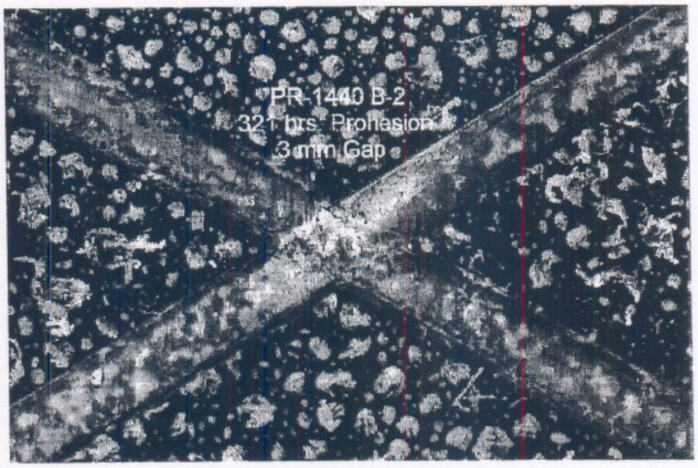
TABLE 8

CORROSION RESISTANCE OF PR-1440 B-2

Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
PR-1440 B-2	153	3 mm	Good	30	9	10
	321	3 mm	Good	40	10	10
	475	3 mm	Good	50	10	10
	643	3 mm	Good	50	7	10
	807	3 mm	Good	90	7	10
	995	3 mm	Good	100	7	10
	153	5 mm	Some	40	9	10
	321	5 mm	Good	50	10	10
	475	5 mm	Some	60	9	10
	643	5 mm	Good	70	9	10
	807	5 mm	Good	95	9	10
	995	5 mm	Good	100	9	10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe

153 hours



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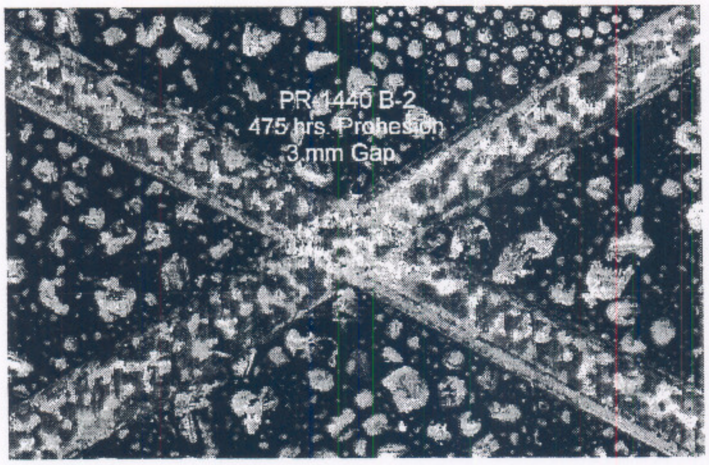

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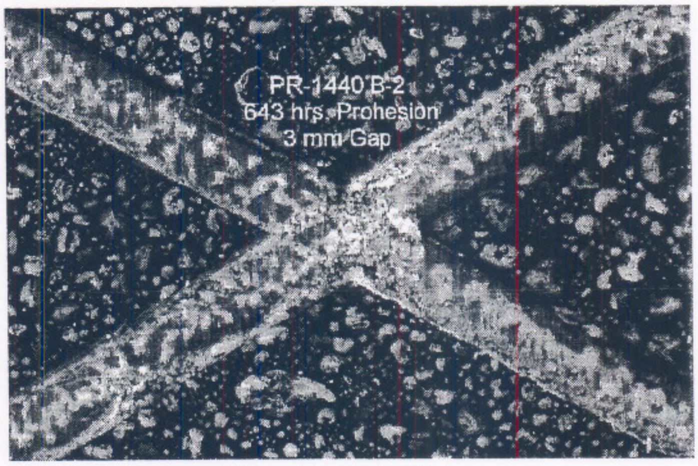
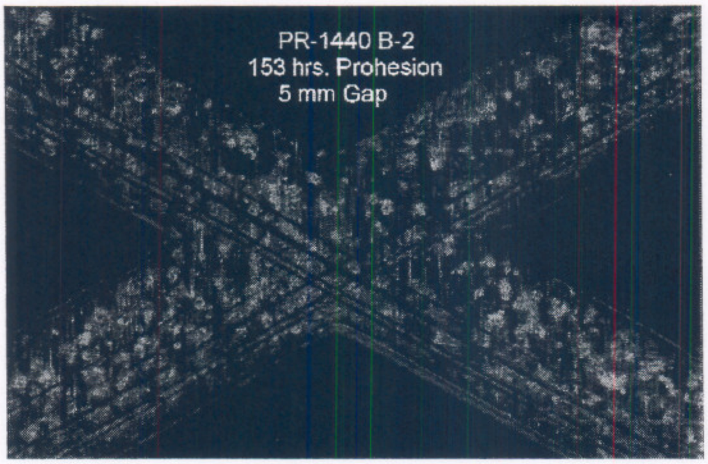


643 hours

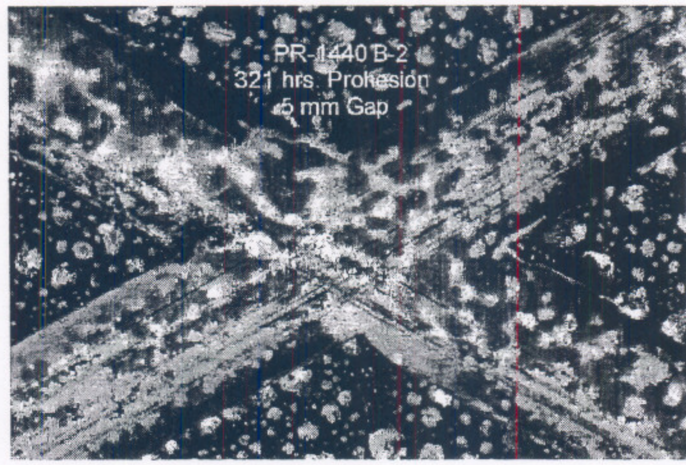
807 hours

995 hours

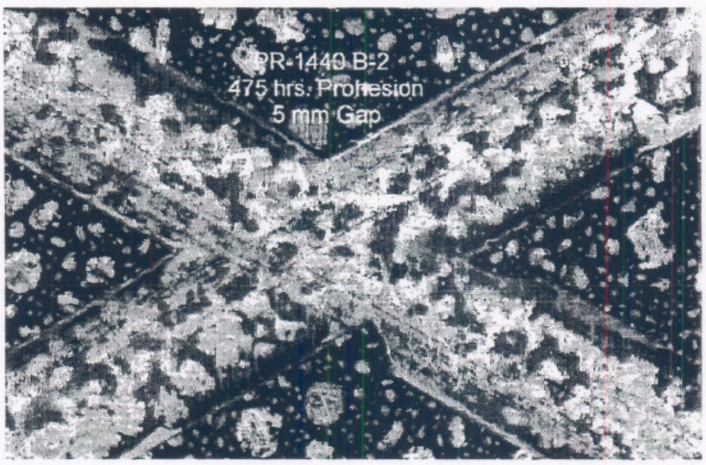
Figure 9. PR-1440 B-2



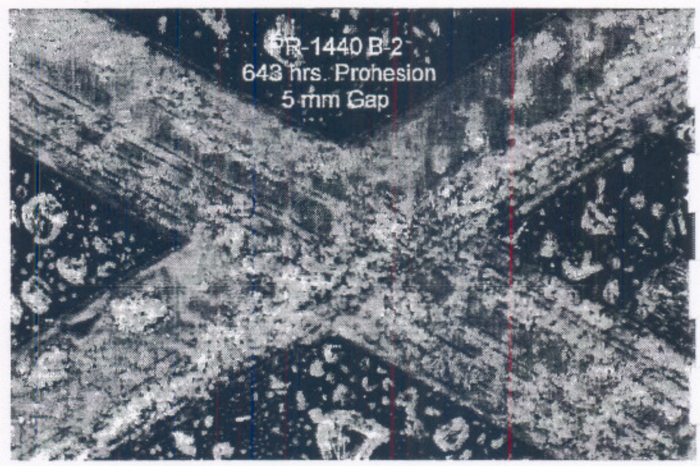
153 hours



321 hours



475 hours



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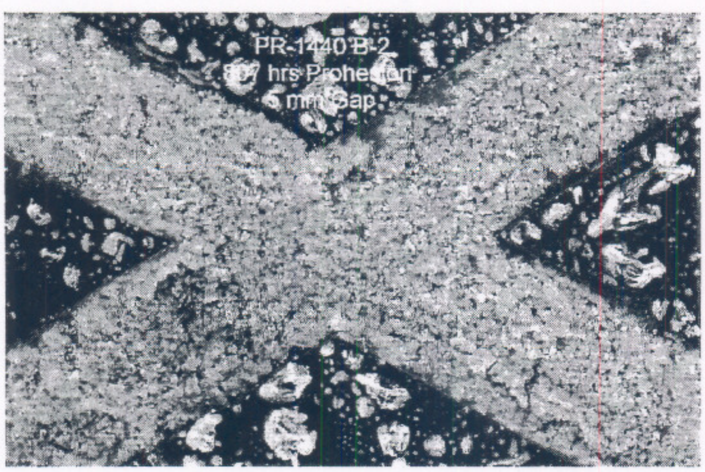
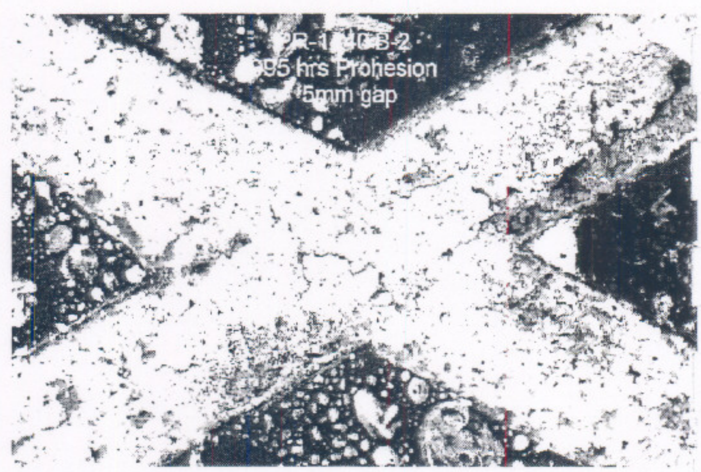


807 hours



995 hours

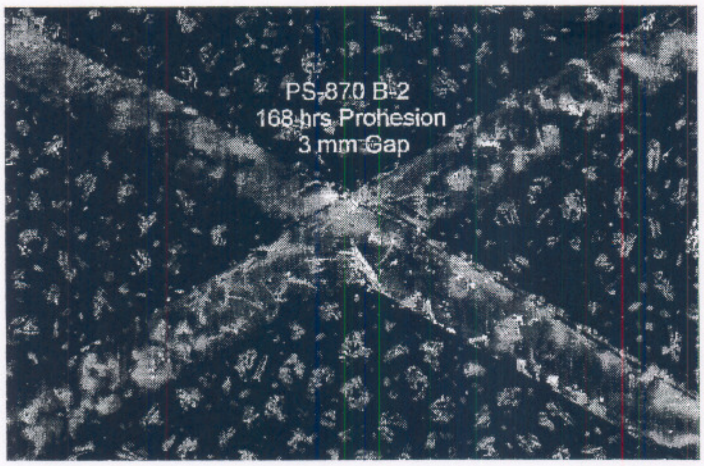
Figure 10. PR-1440 B-2

TABLE 9

CORROSION RESISTANCE OF PS-870 B-2

Material	Time Conditioned (hrs)	Gap Width	Evaluations			
			Adhesion[1]	% Corrosion in Scribe	Procedure A[2]	Procedure B[2]
PR-870 B-2	168	3 mm	Good	25	10	10
	356	3 mm	Some	40	10	10
	504	3 mm	Some	40	8	10
	672	3 mm	Good	90	7	10
	866	3 mm	Blistered	100	0	10
	1008	3 mm	Blistered	100	0	10
	168	5 mm	Good	25	10	10
	356	5 mm	Good	60	10	10
	540	5 mm	Some	60	9	10
	672	5 mm	Good	75	10	10
	866	5 mm	Good	90	10	10
	1008	5 mm	Good	100	10	10

[1] Adhesion Ratings: Good Adhesion, Some Adhesion, Little Adhesion, No Adhesion
[2] See Table 1 (ASTM D 1654) Procedure A-Corrosion under coating @ scribe mark; Procedure B-Corrosion under coating away from scribe



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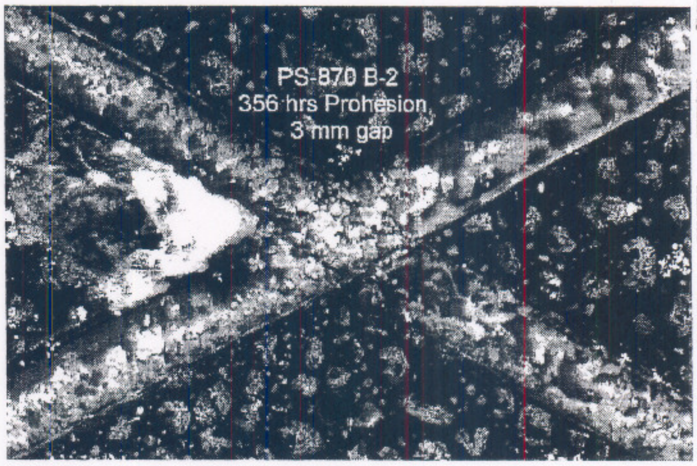
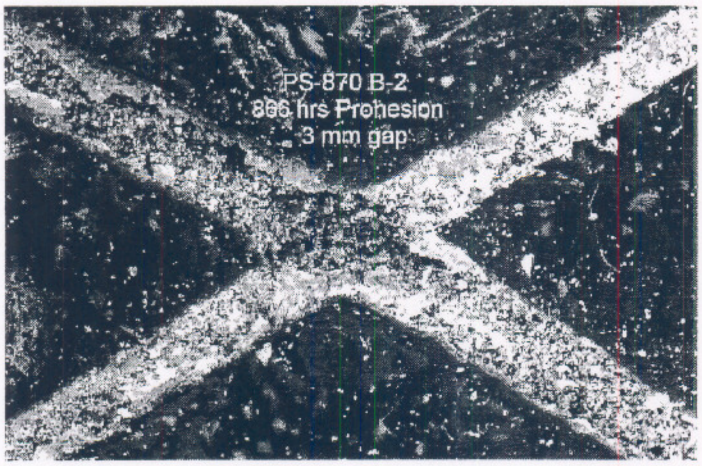


356 hours

504 hours

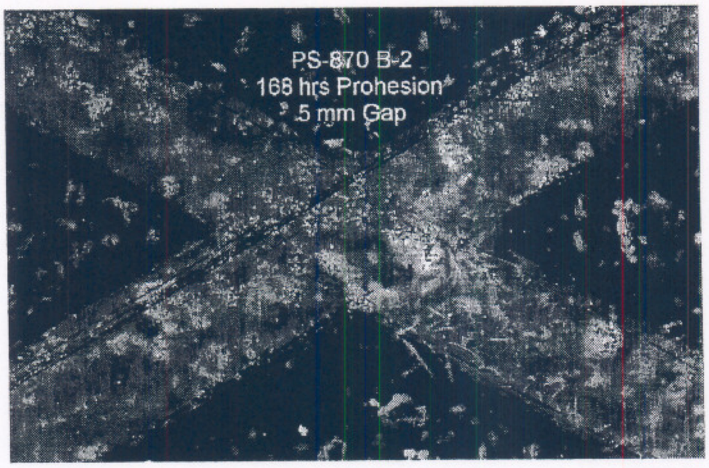
672 hours



866 hours

1008 hours

Figure 11. PS-870 B-2



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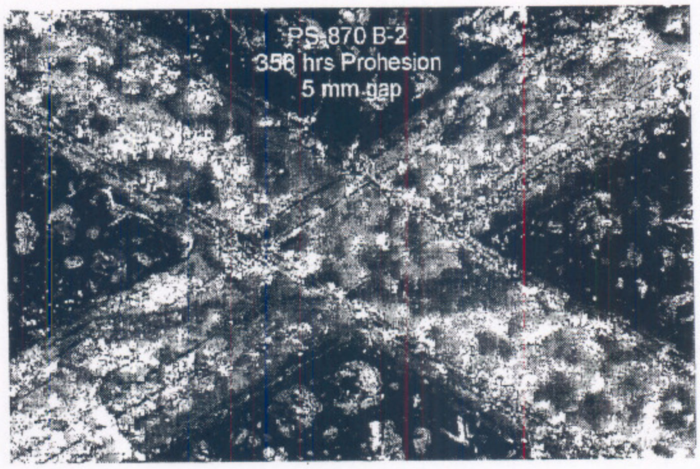

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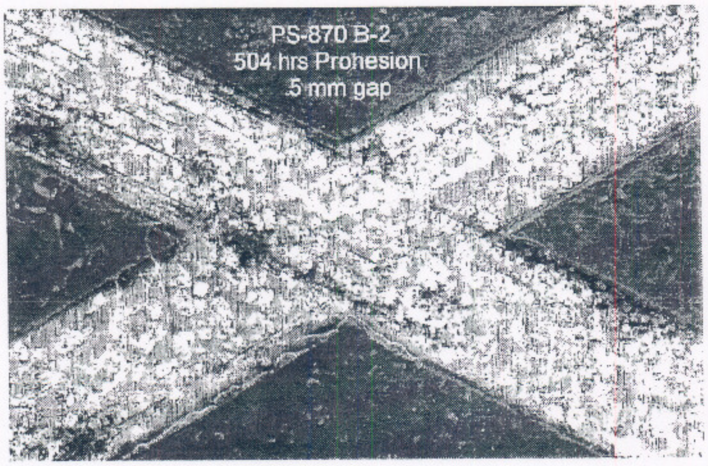
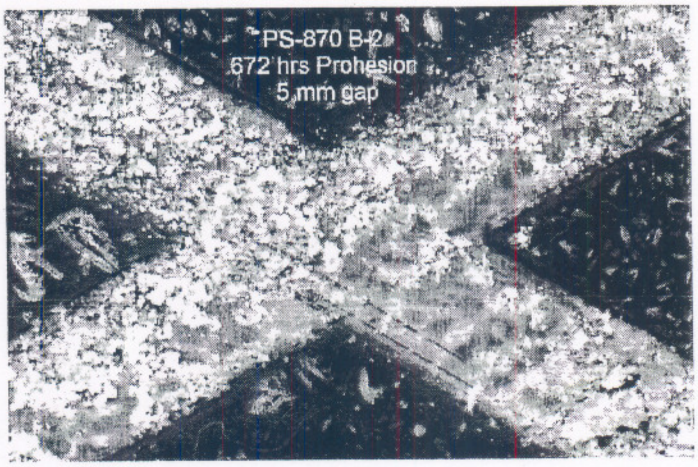
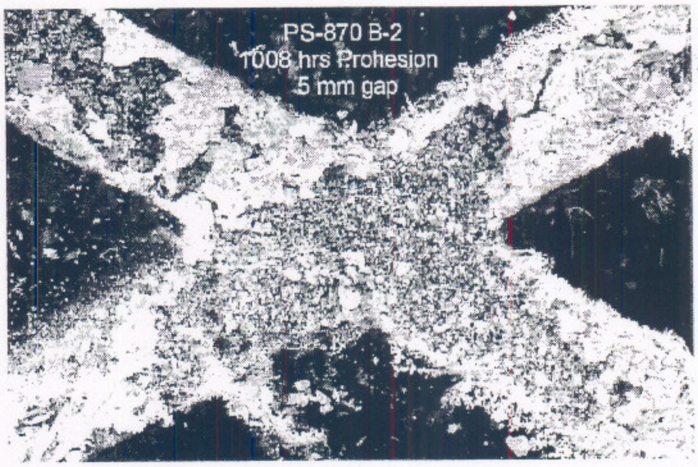


504 hours



672 hours

866 hours



1008 hours

Figure 12. PS-870 B-2

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Figure 13 is the weekly photographs of the AMS 4045 panels that accompanied the sealants in the prohesion chamber.

3.3 SALT FOG TESTING

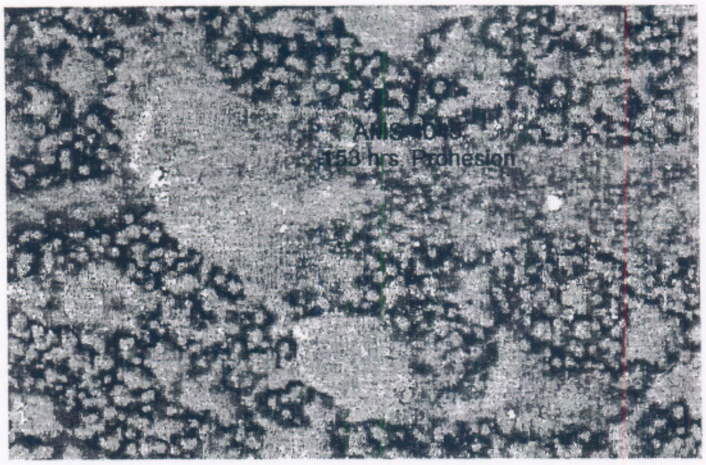
The MIL-PRF-81733D sandwich corrosion test was performed by NAVAIR PAX personnel.

3.3.1 MIL-PRF-81733D Test Procedure

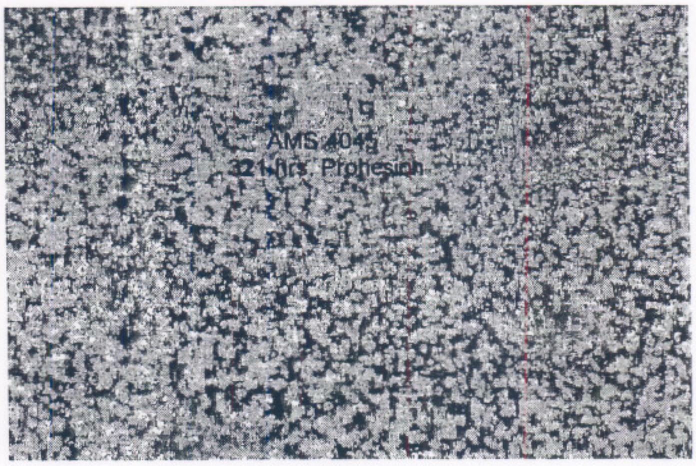
MIL-PRF-81733 (Sealing and Coating Compound, Corrosion Inhibitive) contains instructions and requirements for assembling, testing, and inspecting mixed metal corrosion specimens subjected to a salt-SO_2 fog environment. The specimens, assembled from panels of two different materials insulated from each other by the candidate sealant, create a galvanic cell (anode and cathode) that is bridged by the conductive medium (electrolyte) of the SO_2-salt fog. The "mixed" metals typically used for the assemblies (and specified in MIL-PRF-81733) are aluminum/titanium and aluminum/magnesium. Although graphite/epoxy composites are relatively non-conductive compared to metals, there is enough conductivity in the graphite to generate galvanic potential between itself and aluminum. Given the increased use of graphite/epoxy composites in military aircraft construction, mixed metal corrosion tests frequently include composite/aluminum specimens.

The specifics of the specimens and exposure conditions for the mixed metal corrosion test in MIL-PRF-81733 are detailed here. The anode is a 2" x 3" panel and the cathode is a 4" x 6" panel; both panels are approximately 0.063" thick. Sealant is applied to the mating surfaces of the two panels and they are mated and secured with two non-metallic (nylon) fasteners (total sealant thickness of 0.007" after assembly). After the candidate sealant has completed curing, the specimens are exposed for 4 weeks in a salt-SO_2 spray cabinet. Conditions in the cabinet are specified in ASTM B-117 and include: a 5% by weight sodium chloride solution, cabinet temperature of 95 + 2°F, saturator tower temperature of 115 + 2°F, and sulfur dioxide gas is injected for 1 hour in every 6 hours (four times daily) at a flow rate of $1cc/min/ft^3$ of box. Conditions in the cabinet are monitored by measuring the collection rate of condensate, pH, and specific gravity.

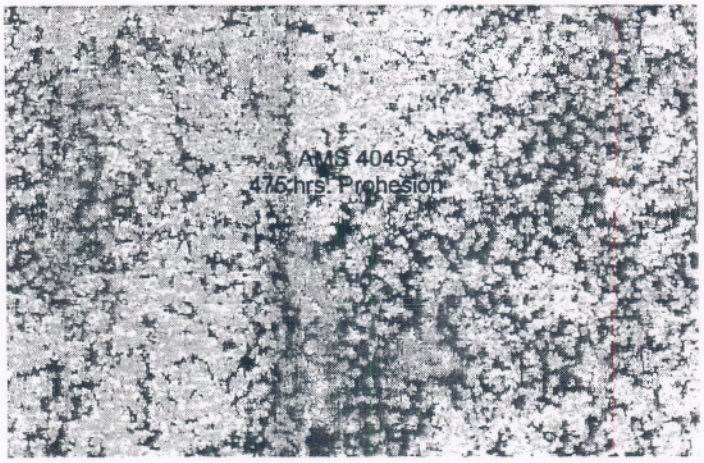
The capability of the candidate sealant to inhibit corrosion between the two panels in the corrosive environment of the salt-SO_2 fog cabinet is evaluated by separating the panels, removing the sealant, and inspecting for corrosion. The requirements for passing



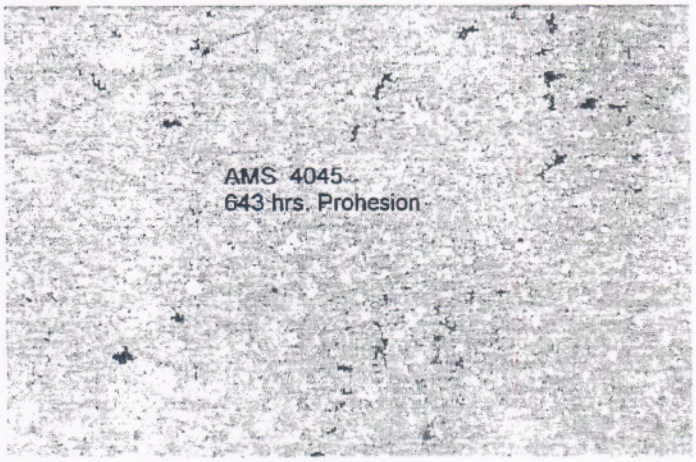
153 hours



321 hours

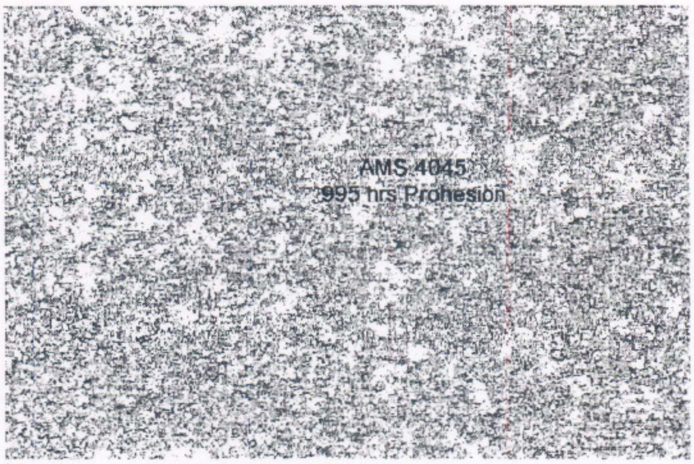


475 hours



643 hours

807 hours



995 hours

Figure 13. AMS-4045 Panels

the mixed metal corrosion test are that the sealant shall not in itself induce corrosion and it must protect the substrate metal such that there is no visible evidence of corrosion at the metal sealant interface.

3.3.2 MIL-PRF-81733 Sandwich Corrosion Test Results

Tables 10 and 11 summarize the results of the MIL-PRF-81733 sandwich corrosion test performed by NAVAIR PAX on the three sealant candidates (RW-3608-68, RW-3609-68, and RW-3610-68) supplied by PRC-DeSoto. Three sandwich panel specimens were made up for each sealant for each of the three anode/cathode combinations (aluminum/magnesium, titanium/aluminum, and AS4/3501-6 composite (GrE)/aluminum). One specimen of each set was exposed in the SO_2-salt fog chamber for 2 weeks and the remaining two specimens were exposed for the full 4 weeks in the chamber. Specimens were removed, rinsed, disassembled, and both panels were inspected for signs of corrosion. The following are several additional comments regarding the test results:

(1) The RW-3608-68 sealant did not cure completely under any of the sandwich panels. This sealant was particularly hard to mix and may not have been mixed fully. As a result, the 2-week specimens demonstrated some minor pitting of the aluminum under the sealant (Al/Mg) and some minor edge discoloration of the aluminum with the composite/aluminum couple. The 4-week results were similar with pitting occurring in the Al/Mg specimens and some edge discoloration with the other couples.

(2) Both the RW-3609-68 and RW-3610-68 sealants did very well with the graphite epoxy/aluminum couple with only minor discoloration (no pitting/ corrosion products) occurring on the aluminum panels.

(3) The RW-3609-68 performed slightly better than the RW-3610-68 sealant with the titanium/aluminum couple; no signs of corrosion were evident with the RW-3609 and only minor edge discoloration and one edge pit noted on the aluminum on one specimen with the RW-3610. Because there was such minimal discoloration on the RW-3610-sealed aluminum panel, the edge pit may have been due to damage to the conversion coating prior to or during specimen fabrication.

(4) With both 4-week specimens for both the RW-3609-68 and RW-3610-68 sealants there were clear failures (per MIL-PRF-81733) with the aluminum/ magnesium couples. In Tables 10 and 11 there is a distinction between pits in the aluminum that were located under the top panel and pits in the aluminum that were located under the sealant fillet around the edge of the panel. While most of the pits were under the sealant fillet, there were also

TABLE 10
4-WEEK CORROSION TEST RESULTS

Sealant/ Substrate	Spec. No.	Corrosion Results	Other Comments
RW-3608-68 Ti/Al	10	Ti: Clean	Tacky, sealant 50/50
		Al: Minor edge discoloration	
	11	Ti: Clean	Tacky, sealant 50/50
		Al: Minor edge discoloration and white corrosion products around one fastener hole	
RW-3608-68 Al/Mg	12	Al: Several medium pits under sealant edges	Tacky, sealant 50/50
		Mg: Large pit ¼" into panel, slight edge discoloration and some edge corrosion	
	13	Al: Several pits under sealant edges	Tacky, sealant 50/50
		Mg: Heavy edge corrosion, edge discoloration	
RW-3608-68 GrE/Al	22	GrE: Clean*	Tacky, sealant 50/50
		Al: Slight edge discoloration	
	23	GrE: Clean	Tacky, sealant 50/50
		Al: Slight edge discoloration	
RW-3609-68 Ti/Al	22	Ti: Clean	70% on Ti
		Al: Clean	
	23	Ti: Clean	90% on Ti
		Al: Clean	
RW-3609-68 Al/Mg	16	Al: Several large pits under sealant edges	90% on Al
		Mg: Edge discoloration	
	17	Al: 2 minor pits under panel, several large pits under sealant edges	95% on Al
		Mg: Edge discoloration	
RW-3609-68 GrE/Al	24	GrE: Clean	99% on GrE
		Al: Clean	
	25	GrE: Clean	95% on GrE
		Al: Some discoloration around fastener hole	

TABLE 10 (Concluded)
4-WEEK CORROSION TEST RESULTS

Sealant/ Substrate	Spec. No.	Corrosion Results	Other Comments
RW-3610-68 Ti/Al	18	Ti: Clean	~ 70% on Ti
		Al: Minor edge discoloration	
	19	Ti: Clean	~ 60% on Ti
		Al: Slight edge discoloration, one edge pit	
RW-3610-68 Al/Mg	20	Al: 10% discoloration, 2 minor pits under panel, several large pits under sealant edges	90% on Al
		Mg: Large area of pitting around one fastener hole	
	21	Al: 2 medium pits under panel, several large pits under sealant edges	95% on Al
		Mg: Large area of pitting around one fastener hole	
RW-3610-68 GrE/Al	26	GrE: Discoloration (may be sealant)	99% on GrE
		Al: Several small spots of discoloration	
	27	GrE: Discoloring (may be sealant)	95% on GrE
		Al: Clean	

TABLE 11

2-WEEK CORROSION TEST RESULTS

Sealant/ Substrate	Spec. No.	Corrosion Results	Other Comments
RW-3608-68 Ti/Al	2	Ti: Clean Al: Clean	Tacky, 50/50
RW-3608-68 Al/Mg	1	Al: Minor pitting under sealant Mg: Clean	Tacky, 70% on Al
RW-3608-68 GrE/Al	7	GrE: Clean Al: Minor edge discoloration	Tacky, 60% on GrE
RW-3609-68 Ti/Al	3	Ti: Clean Al: Clean	90% on Ti
RW-3609-68 Al/Mg	4	Al: 1% discoloration Mg: Edge discoloration	90% on Al
RW-3609-68 GrE/Al	8	GrE: Clean Al: Clean	90% on GrE
RW-3610-68 Ti/Al	5	Ti: Clean Al: Clean	60% on Al
RW-3610-68 Al/Mg	6	Al: Clean Mg: Clean	70% on Al
RW-3610-68 GrE/Al	9	GrE: Minor discoloration under panel (may be residual sealant) Al: Clean	Sealant slightly tacky, 80% on GrE

several pits directly under the panel. The RW-3609 may have performed slightly better as there was only edge discoloration on the magnesium panel vs. large areas of pitting around the fastener holes with the RW-3610.

(5) The percentages under the "other comments" section of Table 10 noted which side the majority of the sealant adhered to when the panels were taken apart. There is certainly no requirement for reporting this detail and no real precedent for comparison but, because the sealants are new and no adhesion testing had been reported, the observations were reported for information only. Because the RW-3608 was still tacky when the specimens were disassembled, the sealant was generally split about 50/50 between the two substrates.

a. The 4-week results were generally more consistent between the sealants than the 2-week results. At four weeks: with the Ti/Al couple, the majority (60-70%) of the sealant (both RW-3609 and RW-3610) remained on the titanium. With the Al/Mg couple, the majority (90-95%) stayed on the Al and with the composite/Al couple, the vast majority (95-99%) adhered to the composite. At two weeks: the Ti/Al results ranged from 40% (RW-3610) to 90% (RW-3609) on the titanium, the Al/Mg results ranged from 70% (RW-3610) to 90% (RW-3609) on the aluminum, and the GrE/Al results ranged from 80% (RW-3610) on the composite.

3.3.3 Conclusions

From the test results of the three candidate sealants, there is no obviously superior choice for greatest corrosion protection. The RW-3608-68 results were inconclusive because the sealant did not cure properly. In testing of both the RW-3609-68 and RW-3610-68 sealants there were clear failures (per MIL-PRF-81733) with the aluminum/ magnesium couples. Both sealants performed well (RW-3609 might have performed marginally better than the RW-3610) with the titanium/aluminum and composite/ aluminum couples with minor discoloration the only visible sign of exposure. It should be noted that one concern with this test has been its general *inability* to distinguish between standard and corrosion-inhibiting sealants (standard sealants usually pass). In previously corrosion tests with several different sealants, the corrosion-inhibiting sealants have not been the best performers. Table 12 includes corrosion test results from a 1995 evaluation and the best performers were "standard" sealants (PR-1826, PR-1829, PR-1750) and the corrosion-inhibiting sealants (PS-870, PR-1775, PR-1875) had significant discoloration at a minimum and with the PS-870, several pits around a fastener hole which constitutes a failure. These failures that were experienced in sandwich specimen testing of the new corrosion-inhibiting sealants, while disappointing, were not inconsistent with previous test results of current corrosion-inhibiting sealants. Use of this test for screening of further candidates, while some differences may be noted, is not recommended.

TABLE 12

CORROSION TEST RESULTS
ALUMINUM/MAGNESIUM COUPLE (1995)

Sealant	Soak Time	Results/Description
PS-870	2 weeks 4 weeks	No discoloration; 1 pit at top edge of sealant 10% discoloration; 2-3 pits around fastener hole
PS-890	2 weeks 4 weeks	1% (light) discoloration; no pits 10% discoloration; no pits
PR-1750	2 weeks 4 weeks	1% discoloration; no pits 2-3% discoloration; no pits but several "holes" in Al at center
PR-1755	2 weeks 4 weeks	No discoloration; no pits 10% discoloration; no pits but several shallow "shiny" spots at edge of discoloration
PR-1776	2 weeks 4 weeks	No discoloration; no pits No discoloration; 3 pits at edge of sealant
PR-1820	2 weeks 4 weeks	1% discoloration; no pits 10% discoloration (light); no pits
PR-1826	2 weeks 4 weeks	No discoloration; no pits No discoloration; no pits
PR-1828	2 weeks 4 weeks	10% discoloration; no pits 10-12% discoloration; no pits but several shallow "shiny" spots at edge of discoloration
PR-1829	2 weeks 4 weeks	No discoloration; no pits but several "holes" in center No discoloration; no pits
PR-1875	2 weeks 4 weeks	No discoloration; no pits No discoloration; 1 pit at edge of sealant

SECTION 4
CONCLUSION

The corrosion protection of the three sealant blends, RW-3607-1/RW-3608-68, RW-3607-1/RW-3609-68, and RW-3607-1/RW-3610-68 was much better than the three control sealants. All panels were protected from corrosion beneath all six sealants, however, the three sealant blends protected the metal in the 3-mm and 5-mm scribe marks and at the scribe lines. The RW-3607-1/RW-3610-68 had the best adhesion properties and corrosion protection of the three sealant blends, although it did not have as good application properties as the RW-3607-1/RW-3608-68, RW-3607-1/RW-3609-68 blends.

APPENDIX C

US ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND REPORT

A Limited Survey of Army Aircraft and Tactical Shelters Using Corrosion Inhibiting Sealants/Coatings

Donald T. Rorabaugh
Dean A. Martinelli

January 2002

US ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

Warheads, Energetics & Combat-support Armament Center

Picatinny Arsenal, New Jersey

Acknowledgement

Much of the descriptive information for the various aircraft listed in this report was obtained from the "US Military Aircraft" (Military Analysis Network) Web Site maintained by The Federation of American Scientists.

Federation of American Scientists
1717 K Street., NW, Suite 209
Washington, DC 20036
(202) 546 – 3300
(202) 675 – 1010 FAX
fas@fas.org
WEB SITES: Home: http://fas.org/index.html
Military Aircraft : http://fas.org/man/dod-101/sys/ac/

Information concerning the various types of DoD Standard Family of Tactical Shelters was obtained from: the US Army Natick Research, Development and Engineering Center, ATTN: SATNC-WST, Soldier Systems Command, Natick, Massachusetts 01760

Introduction

This task is being conducted in support of the SERDP sponsored Pollution Prevention Project PP – 1075, "Replacement Non-Toxic Sealants for Standard Chromated Sealants and Repair"*.

Background

Current aircraft and other military materiel systems (vehicles, shelters, etc.) utilize sealants/coatings such as MIL – PRF – 81733, "Performance Specification Sealing and Coating Compound, Corrosion Inhibitive", to prevent moisture entry, seal fuel tank and other container and/or pressurized areas, provide corrosion protection, and/or provide electrical insulation. Chromium, the primary corrosion inhibiting component currently used in many sealants/coatings, is a hazardous material that current and pending OSHA regulations are aimed at reducing and ultimately removing from the environment. These currently used sealants and coatings also usually contain significantly high concentrations of environmentally unfriendly highly volatile organic compounds (VOC's), which are released into the atmosphere as the sealants/coatings cure.

MIL – PRF – 81733

As of this writing, the current edition of this specification, which is approved for use by all Departments and Agencies of the Department of Defense, is MIL – PRF – 817733D dated 15 May 1998, which supercedes MIL – S – 81733C dated 13 March 1980. This specification covers accelerated, room temperature curing of synthetic rubber compounds used in the sealing and coating of metal components on weapons and aircraft systems for protection against corrosion. The sealing compound can be furnished in two classes and four types. The Class 1 polysulfide synthetic rubber based sealing compound is effective over a continuous operating temperature range of – 65°F to + 250°F (– 54°C to + 121°C). The Class 2 polythioether synthetic rubber based sealing compound is effective over a continuous operating temperature range of – 80°F to + 320°F (– 62°C to + 160°C). Type I is for brush or dip application, Type II is for extrusion application (gun or spatula), Type III is for spray gun application, and Type IV is for faying surface application (gun or spatula).

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* Project Manager: Mr. Alan Fletcher, AFRL/MLSA, Wright-Patterson Air Force Base, OH 45433-7718. (937) 255 – 7481 Alan.fletcher@ml.afrl.af.mil

Objective

The objective of the overall PP-1075 program is to develop non-chromated sealants/coatings that meet the requirements of MIL – PRF – 81733. This is being accomplished by formulating and

testing candidate non-chromated sealants/coatings to achieve properties that are equivalent or superior to the properties of existing chromate containing sealants/coatings described in the subject MIL specification. An additional objective is to reduce the VOC content of the replacement materials by 65 percent or more. The benefits of developing non-chromated, low VOC sealants/coatings will be: a significant reduction in hazardous material handling and waste disposal costs, a major reduction in hazardous VOC emissions, and better health and safety conditions for personnel using the solvents.

Specifically, the ongoing efforts discussed in this report are aimed at finding situations where the non-toxic sealants/coatings , being developed in this overall PP – 1075 program, could be substituted for the MIL – PRF – 81733 chromated seating compounds currently being used for military (Army) applications.

Discussion

QPL – 81733-8

In addition to the military specification, MIL – PRF – 81733, that describes and defines the various versions of corrosion inhibiting compounds, there also is a Qualified Products List (QPL). QPL – 81733-8 dated 16 January 1992, "Qualified Products List of Products Qualified Under Military Specification MIL – S – 81733, Sealing and Coating Compound, Corrosion Inhibitive", lists the compounds that have been officially tested and qualified for used "… by or for the Government in acquisition of products covered by the subject specification. Note that the QPL title references the no longer current MIL – "S" version of the 81733 specification. This "problem" is taken care of in the opening paragraph of the QPS:

> "All products listed herein have been qualified under the requirements for the product as specified in the latest effective issue of the applicable specification. This list is subject to change without notice; revision or amendment of this list will be issued as necessary. The listing of a product does not release the supplier from compliance with the specification requirements."

Thus the QPL items should still meet the revised MIL – PRF – 81733 specification, or the QPL also would have been revised. All of the sealing and coating compounds listed on the QPL are manufactured by PRC Aerospace Sealants/coatings *.

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*PRC, 5454 San Fernando Road, Box 1800, Glendale, CA 91209 (818) 240 2060

The PRC sealing and/or coating compounds listed on QPL 81733 –8 are:

Type I	P/S 870 A
Type I	PR 1440G
Type IV	P/S 870 C
Type IV	PR 1431G

Type IV	PR 1440G

According to PRC representatives, the company has cancelled PR 1431G and PR 1440G. They indicated that the following materials are being certified by them as meeting MIL – PRF – 81733:

Type I	P/S 870 A
Type II	P/S 870 B
Type III	PR 1436G Spray
Type IV	P/S 870C

Applications

One of the primary military applications for corrosion inhibiting sealants and coatings is for aircraft. Specific sealant/coating applications include: fuel resistant fuel tank sealants, cabin/plane pressure seals, windshields, firewalls/bulkheads, aero fairings, access panels, and other areas requiring environmental protection. It is also reported that corrosion-inhibiting sealants/coatings are being used for other military applications, such as vehicles and shelters. In addition to replacing chromate sealants/coatings on the items that are being/to be manufactured, the non-toxic replacement materials also can be used on the many fielded items that are being refurbished and upgraded.

Army Aircraft

As will be noted in the discussion, some of the transport aircraft used for Army applications are maintained by the Air Force. In addition, there often are several variations of some of the Army helicopters that are listed; some of these design variations are used by other service groups, such as the Navy. In addition to the original usage of the corrosion inhibiting sealants/coatings on the various aircraft listed below, it should be noted that additional material is/will be needed as these aircraft are subjected to routine maintenance and, in some cases, to a planned service life extension – modernization program. Newly designed and manufactured aircraft also will require corrosion resistant sealants/coatings.

Helicopters

Some of the Army helicopters requiring corrosion resistant sealants/coatings are listed below:

AH-64 Apache

The AH-64 Apache is the Army's primary attack helicopter. The Apache is a twin-engine, four bladed, multi-mission attack helicopter designed to fight and survive during the day, night, and in adverse weather throughout the world. The Apache has a full range of aircraft survivability equipment and the ability to withstand hits from rounds up to 23mm in critical areas. The AH-64 fleet consists of two aircraft models, the AH-64A and the newer Longbow Apache (LBA), AH-64D. AH-64 A model full-scale production began in 1983 and now over 900 aircraft have been delivered to the US Army and other NATO Allies. The AH-64A fleet exceeded one million flight hours in 1997, and the median age of today's fleet is 9 years old and 1,300 flight hours.

The US Army plans to remanufacture its entire AH-64A Apache fleet to the AH-64D configuration over the next decade.

UH-60 Black Hawk

The Black Hawk is the Army's front-line utility helicopter; it is used for air assault, air cavalry, and aero-medical evacuation units. In addition, modified Black hawks operate as command and control, electronic warfare, and special operations platforms. The UH-60A was developed to replace the UH-1 "Huey" helicopter in the combat assault role.

Elements of the US Army Aviation UH-60A/I Black Hawk helicopter will begin reaching their service life goal of 25 years in 2002. A Service Life Extension Program is scheduled in order for the fleet to remain operationally effective through the time period 2025 – 2030. The aircraft will need to go through and inspection, refurbishment, and modernization process that will validate the structural integrity of the airframe, incorporate improvements in sub-systems so as to reduce maintenance requirements, and modernize the mission equipment and avionics to the levels compatible with Force XXI and Army After Next (AAN) demands.

Variations for the Army's UH-60 Black Hawk include the UH60L (upgraded engines), EH-60A/E (electronic countermeasures), UH-60Q (medevac), MH-60G/HH-60G (Air Force Pave Hawk – Special Ops), and CH-60 Sea Hawk (Navy).

As with the Army's UH-60A/I fleet, the Air Force's HH-60G fleet is rapidly approaching its flying hour service life limit. Consequently, the Air Force soon will require either a service life extension program or procurement of a replacement aircraft for their special ops missions.

OH-6A Cayuse/AH-6J/MH-6J Little Bird/Defender 500

The OH-6A was designed for use as a military scout for the Vietnam War to meet the Army's need for an extremely maneuverable, light, observation helicopter (LOH program). The Cayuse was quite effective when teamed up with the AH-1G Cobra attack helicopter as part of what were known as "Pink Teams". Two special operations versions of the OH-6A are the AH-6J, Little Bird (armed attack version), and the MH-6 Little Bird (insert/extraction - transport/utility version). The defender 500 is the foreign military sales helicopter offered in several versions.

RAH-66 Comanche

The RAH-66 Comanche is the Army's next generation armed reconnaissance helicopter. It also is the first helicopter developed specifically for this role. The Comanche will provide Army Aviation the opportunity to move into the 21st century with a weapon system of unsurpassed war fighting capabilities crucial to the Army's future strategic vision. The Comanche is intended to replace the current fleet of AH-1, OH-6A, and OH-58A/OH-58C helicopters in all air cavalry troops and light division attack helicopter battalions, and supplement the AH-64 Apache in heavy division/corps attack helicopter battalions. Six early operational capability air craft are scheduled to be delivered 2002 to participate in an Army field exercise in 2002-2003, or possibly later in "corps 04"

CH-47 Chinook

The CH-47 Chinook, designated the Army's Medium Transport Helicopter, is a twin engine, tandem rotor helicopter designed for transportation of cargo, troops, and weapons during day, night, visual, and instrument conditions. It also performs rescue, aero medical, parachuting, aircraft recovery, and special operations missions. The current CH-47D model is a modernized version of the prior "A", "B" and "C" models. During Desert Storm the CH-47D was often the only mode of transportation to shift large numbers of personnel, equipment, and supplies rapidly over the vast area in which the US forces operated. MH-47D and MH-47E are specially modified Chinooks in the Army inventory used for special operations; they have significantly increased fuel capacity, and are air refuelable.

Current efforts center around the Improved Cargo Helicopter (ICH). The ICH is a remanufactured version of the CH-47D Chinook cargo helicopter. Airframes will be restored to their original condition and the air crafts life is expected to be extended another 20 years to the 2025-2030 time frame.

AH-1 Cobra

The AH-1 Cobra is an attack helicopter capable of performing its missions in all weather conditions; these include direct air support, antitank, armed escort, and air to air combat. 1,100 of the Army's AH-1G aircraft logged over 1 million hours in Vietnam. The Marine Corps utilizes the AH-1J version (Sea Cobra) along with the upgraded AH-1W twin engine, Super Cobra capable of land or sea operations.

A four bladed version of the AH-1W, designated AH-1Z, is under development. In addition, the Marine Corps plans to upgrade their AH-1W gun-ships to the new AH-1Z standard. Low rate initial production is expected to begin in February 2002, with deliveries running from 2004 through 2013.

UH-1 Huey

The UH-1 "Huey" is the most widely used military helicopter in the world. It is used for medevac, command and control, personnel and materiel transport, air assault, and a gun ship. More than 5,000 of these versatile aircraft were used in the Southeast Asia conflict. Several upgrades were made along with the development of the UH-1N Navy version.

The Marine Corps is upgrading the UH-1N to achieve a platform that meets their future operational needs.

OH-58D Kiowa Warrior

The OH-58D Kiowa Warrior is an armed reconnaissance helicopter that also can be utilized for air combat, artillery target designation work, and limited attack operations. The OH-58D is the armed version, of the earlier OH-58A/C models.

The Army's procurement plan is to acquire, through modification or retrofit of existing OH-58A and D aircraft, approximately 500 Kiowa Warriors.

Air Transport

C-5A/B Galaxy

The C-5 Galaxy, one of the world's largest aircraft, is a heavy-cargo transport designed to provide strategic airlift for deployment and supply of Army and other DoD combat and support forces. The C-5 can carry unusually large and heavy cargo for intercontinental ranges at jet speeds. The C-5 and C-141B Starlifter are strategic partners. Together they can carry fully equipped, combat ready troops to any area of the world on short notice and provide full field support necessary to maintain that fighting force.

The Air Force is conducting a multiphase modernization/refurbishing effort to upgrade the C-5 Galaxy. Service life is effected by things such as system obsolescence, reliability and maintainability, impacts of corrosion, and required repairs. Currently, the C-5 has the highest operating cost of any DoD weapon system.

C-17 Globemaster III

The C-17 Globemaster III is the newest airlift aircraft in the Air Force's inventory. It is capable of rapid strategic delivery of Army troops and all types of cargo to main operating bases or directly (air drop) to forward bases in the deployment area. The aircraft also is able to perform theater airlift missions when required.

Based on a buy of 120 aircraft, the last C-17 delivery is scheduled for November 2004. The original specification defined a service life of 30,000 hours. Modification/upgrade refurbishing programs will keep this aircraft in line with current and future requirements such as: threat avoidance, navigation, communication and enhanced capabilities.

C-23 Sherpa

The C-23 Sherpa is the Army National Guard's answer to missions requiring an aircraft that is capable of faster, higher-altitude and longer-distance coverage that helicopters. The C-23 multi-role utility airplane is the only cargo airplane in the Army's inventory.

C-141B Starlifter

The C-141 Starlifter is a stretched C-141A with in-flight refueling capability. It is the workhorse of the Air Mobility Command, fulfilling a vast spectrum of airlift requirements through its ability to airlift combat forces over long distances, inject those forces and their equipment either by airland or airdrop, resupply employed forces, and extract the sick and wounded from hostile areas to advanced medical facilities.

The C-141 currently is undergoing modifications aimed at preserving the current force by reliability and maintainability improvements and capability improvements necessary for effective use through 2006.

DoD Tactical Shelters

DoD defines a tactical shelter as a presized, transportable (land, sea, and air) structure designed for a functional requirement and which provides a live-in or work-in capacity. This structure can be either non-expandable or expandable. In so far as practical, the shelter will conform to applicable ANSI/ISO container standards. These shelters are complete units that require no specialized set-up equipment and minimum site preparation. Tactical shelters exclude fabric wall shelters, air supported structures, refrigerated buildings, cargo containers, and prefabricated semi-permanent buildings/structures.

The DoD standard family of tactical shelters, utilizing polysulfide materials (DODI 4500.37) is listed below:

Non Expandable Shelter (Class 1)	Nat. Stock Number
6 x 6 x 7 Army S-250/G EMI	5411-00-489-6076
7 ¼ x 7 ¼ x 12 Army S- 280 C/G	5411-01-092-0892
5'7" x 7 x 8 ½ Army SICPS, Integrated, S-787/G	5411-01-333-5941
5'7" x 7 x 8 ½ Army LTWT, Multipurpose, S-788/G	5411-01-357-3582
8 x 8 x 10 ISO Marine Corps EMI	5411-01-206-6079
8 x 8 x 10 ISO Marine Corps GP	5411-01-287-4341
8 x 8 x 20 ISO Naval Mobility Facility	5411-01-355-4322
8 x 8 x 20 ISO Marine Corps GP	5411-01-209-3451
8 x 8 x 20 ISO Marine Corps EMI	5411-01-206-6078
8 x 8 x 20 ISO Army 60 AMP, S-781/G	5411-01-136-9837
8 x 8 x 20 ISO Army 100 AMP, S-786/G	5411-01-294-6390

Expandable Shelter (Class 2)	Nat. Stock Number
7 ½ x 7 ¼ x 12 Air Force S-530 A/G	5411-01-072-2517
8 x 8 x 20 ISO Army 1-side exp. 60 AMP, S-783/G	5411-01-124-1377
8 x 8 x 20 ISO Army 1-side exp.100 AMP, S-784/G	5411-01-295-3433
8 x 8 x 20 ISO Army 2-side exp. 60 AMP, S-785/G	5411-01-136-9838
8 x 8 x 20 ISO Army 2-side exp.100 AMP, S-786/G	5411-01-294-9866

Highly Expandable Shelter (Class 3)	Nat. Stock Number
8 x 8 x20 ISO Army-Air Force Modular Extendable Shelter Kit	5411-01-206-6077

Knock down (Class 4)	Nat. Stock Number
8 x 8 x 20 ISO Marine Corps	5411-01-206-6077

Future Work

Future efforts will be aimed at determining the quantity of MIL – PRF – 81733 type sealants/coatings utilized in the various Army materiel items listed above along with possible vehicular applications for these materials with the overall aim of replacing chromated and/or high VOC materials with the non-toxic, chromate free low VOC sealants/coatings being developed under this SERDP sponsored PP-1075 program.

APPENDIX D

ENVIRONMENTAL PROTECTION AGENCY WHITE PAPER

Replacement Non-Toxic Sealants for Standard Chromated Sealants
PP-1075

White Paper Detailing U.S. EPA Contributions to Project

Heriberto Cabezas, Ph.D.
Leader, Simulation and Design Team
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
Tel. 513-569-7350
Fax 513-569-7111
cabezas.heriberto@epamail.epa.gov

1. Overall Primary Task

The primary task of the U.S. EPA component of the research team will be to help design solvent systems which are environmentally better and have good technical performance for use with the new non-toxic sealants. Solvents are needed for various functions such as formulating, applying, curing, and removing sealants. U.S. EPA personnel will, therefore, work closely with other members of the research team to design solvents that are appropriate to the new sealants.

2. PARIS II Solvent Design Software

The project capitalizes on already existing expertise in solvent design at the U.S. EPA's National Risk Management Research Laboratory. Research engineers at the U.S. EPA, Drs. Heriberto Cabezas and Renhong Zhao in collaboration with Subba Nishtala of the Research Triangle Institute, have developed a very sophisticated computer program, PARIS II, for the design of environmentally better replacement solvents. PARIS II is an acronym for Program for Assisting the Replacement of Industrial Solvents, Version 2. The solvent design algorithm and the core code were developed internally at the U.S. EPA. The graphical user interface for the program was developed at the Research Triangle Institute. Thus, the technical expertise that is relevant to the sealant project resides within the National Risk Management Research Laboratory at this point.

The PARIS II software uses static, dynamic, safety, and environmental properties to design replacement solvents. These properties characterize all of the behavior of solvents so that the behavior of the replacement maps into the behavior of the original solvent irrespective of application. The static properties are divided into solution properties which consist of molecular mass, density, boiling point, vapor pressure, and surface tension, and solvent performance properties which consist of six infinite dilution activity coefficients. The activity coefficients are calculated for six hypothetical solutes (ethanol, diethyl ether, acetone, water, octane, and benzene) representing six different chemical families (alcohols, ethers, ketones, water, normal hydrocarbons, and aromatics). Since one does not often know the solutes that a given solvent will encounter, these six hypothetical solutes serve as proxies for all solutes.

In a more detailed sense, the static solution properties are related handling and operating with the solvent, and the static performance properties are related to the molecular interactions between the solvents and its solutes, i.e., to the ability of the solvent to perform it basic solvent function such as dissolving solutes. The latter define the basic usefulness of the solvent and are, therefore, somewhat more important than the former. The dynamic properties used are the viscosity and the thermal conductivity. The safety property is the flash point. The environmental properties are represented by two indexes: an overall environmental index and an air index representing VOC's. The PARIS II software includes a comprehensive suite of well-tested property prediction routines from the literature (Zhao and Cabezas, 1998; Cabezas et al., 1999) for all the static, dynamic, and safety properties. It is, thus, only necessary to know the identity of pure chemical solvents and the composition in the case of mixtures. There is no need for the user to have values for any of the aforementioned properties. PARIS II essentially designs replacement solvents by looking for pure chemicals or mixtures that have properties close to those of those of the original solvent. It should be noted, however, that for the two environmental indexes, the values for the current solvent are treated not as desired values but as an upper bound. The desired value for these indexes is zero because, all other things being equal, the lower the value of the environmental indexes the better the solvent. PARIS II will, therefore, tend to design solvents that are environmentally better than the original solvent.

3. Solvent Environmental Impacts

The aforementioned environmental and air indexes will be used in the sealant design effort. These are calculated using a data base of basic environmental impact information, e.g., LD50's, LC50's, threshold Limit Values, etc., for the 1600+ most commonly used chemicals across eight potential environmental impact categories. The impact categories consist of two human toxicological effects (human toxicity potential by ingestion and human toxicity potential by inhalation/dermal exposure), two ecological effects (aquatic toxicity potential and terrestrial toxicity potential), two regional effects (acidification potential and photochemical, i.e., smog, formation potential), and two global effects (ozone depletion potential and global warming potential). The overall environmental index , ψ_i, for a pure chemical i is given by,

$$\psi_i = \sum_{j=1}^{8} \alpha_j \psi_{ij}^s \qquad (1)$$

where the sum is taken over the aforementioned eight categories, α_j is the relative weight of impact category j, and ψ_{ij}^s is the specific normalized score of chemical i in impact category j obtained from the database. ψ_{ij}^s has units of potential environmental per kilogram of i, and it is normalized such that the score of the average chemical in the database is 1. The α_j's allow us to construct environmental profiles for different uses of solvents. For example, if the solvent comes into contact with the skin of human workers, then it is prudent overweight human toxicity potential by dermal exposure and so on. For solvent mixtures, the overall environmental index is given by a weight additive rule,

$$\psi_m = \sum_k W_k \psi_k \qquad (2)$$

where the sum is taken over all components k, W_k is the mass fraction of chemical k, and ψ_k is calculated from Eq. 1.

The air index ψ_i^{air} of a chemical i is calculated by multiplying the index ψ_i of each chemical i by its normalized fugacity. For pure chemical solvents the expression is,

$$\psi_i^{air} = \frac{P_i^v \psi_i}{P} \tag{3}$$

where P_i^v is the vapor pressure of i, P is the pressure, and ψ_i is calculated from Eq. 1. For solvent mixtures the appropriate expression for the air index ψ_m^{air} of mixture m is,

$$\psi_m^{air} = \frac{\sum_i x_i \gamma_i P_i^v \psi_i M_i}{P \sum_i x_i M_i} \tag{4}$$

where the sum is taken over all components i, x_i is the mile fraction of component i, γ_i is the activity coefficient of component i, M_i is the molecular mass of component i, and the other symbols have their previously assigned interpretation. The air index is a combination of the potential environmental impact of each chemical component and its tendency to evaporate. Eq. 4 includes the non-idealities of liquid mixtures which can make the volatility of pure chemicals vary when these are combined into mixtures. This is embodied in the activity coefficient γ_i, and it can be extremely important because γ_i can range from near zero to thousands.

4. Solvent Design for Sealants

Using the ideas from the PARIS II software for the design of aerospace sealants involves three separate steps: (1) modification of PARIS II itself, (2) design of new solvents, and (3) testing and validation of the new solvent designs. This process will very likely be iterative with the results from validation and testing feeding back to the solvent design.

Modifying the PARIS II software to design solvents for specific sealants is relatively straightforward. This modification should involve the following three steps:

(i) Establish the molecular structure of the proposed sealants whether that be a polysulfide, a polythioether, or some other structure. This information we would need to obtain from other members of the research team.

(ii) Develop a list of the properties that are deemed relevant to the design of solvents for use with sealants. This list of properties needs to be developed in collaboration with other teams members. Many of these properties already exist in the PARIS II software, but some will have to be added. Some properties may not be important here, and they will be deleted. For example, it is likely that the rate at which the solvent evaporates from the sealant will have to be added. In the process of designing the solvent, one could, incidentally, tailor the evaporation rate to enhance the properties of the sealant surface.

(iii) Modify the activity coefficient routine to reflect only the sealant since in this case, the solute is the sealant, and there is no need for the aforementioned proxy solutes.

The design of the new solvents is a relatively simple exercise. We simply need to know what sealants are being considered, and we then need design the appropriate solvents. These are custom designed solvents tailored to specific sealants. This work will be done at the same rate at which new sealants are developed for consideration. We will, however, need to do this in close

collaboration with the other team members. The reason is that it is critical that the solvents that we design "make sense" in the context of sealant application and use. There are always practical questions such as cost or experience that may or may not be adequately captured in a computer program. It is important to understand, however, that our computer-aided solvent design approach has great flexibility can not be found elsewhere. For example, if there is a particular chemical that is not a desirable solvent component, e.g., it is listed in the Toxic Release Inventory or experience indicates that it has some other specific hazard, it is almost always possible to use our computer-aided approach to design an alternative solvent skipping the undesirable chemical. Doing this by any other means that we are aware of is not possible.

The testing and validation of the proposed solvents will be done together with sealants, i.e., the entire sealant-solvent system needs to be tested together. The testing will be done by other team member according to the work plan. The results of these test will be used by the U.S. EPA part of the team to recommend or reject solvents, to design new solvents and to further modify the and improve the solvent design software.

5. Expected Results

The expected results from this project are a series of technically effective and environmentally better sealant-solvent systems for wide use in aerospace applications with effective custom designed solvents.

6. Personnel

Heriberto Cabezas, Ph.D., Chemical Engineer and Leader of the Simulation and Design Team, National Risk Management Research Laboratory, U.S. EPA

Dr. Meirong Li, Chemical Engineer, Research Associate, National Research Council

Dr. Renhong Zhao, Chemical Engineer, Research Fellow, Oak Ridge Institute for Science and Education

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APPENDIX E

NAVAL AIR WARFARE CENTER (NAWC) TEST REPORT

APPENDIX E

Initial Physical/Application Property Test Results
For RW-3758-71 B-2 (Lot # RT-0904) Submitted to NAWC

TEST PARAMETER	REQUIREMENT		RESULT
	AMS-3265	**MIL-PRF-81733**	
Specific gravity, max.		1.5	1.5
Hardness (Shore A)	40, min. (after 14-day cure)	35, min. (after 14-day cure)	48
Hardness (Shore A)	30, min. (after 72 hours)		
Non-Volatile Content, min.	92%	92%	96%
Application Time, at 2 hours	>15 g/min	>15g/min	62 g/min
Tack Free Time, max.	24 hours	12 hours for Class 2	>24 hrs (likely greater than 48 hrs)

Initial Tensile/Elongation Test Results
For RW-3758-71 B-2 (Lot # RT-0904) Submitted to NAWC

TENSILE/ELONGATION	REQUIREMENT		Tensile (psi)	% Elong
	AMS-3265	**MIL-PRF-81733**		
Standard Baseline	200/200%	250/250%	428	127
12 Day JRF @ 140F	200/200%		388	95
12 days @ 140F, 60 hrs @ 160F, 6 hrs @ 180F (in JRF)	125/100%		393	94
12 days @ 140F, 60 hrs @ 160F, 6 hrs @ 180F (in JRF) + thermal cycle	25/100%		132	25
Standard Heat Cycle (six cycles of 4 hrs @ 260°F + 40 min @ 320°F + 1 hr @ 360°F)	200/100%		134	34

Initial Peel Strength Test Results
For RW-3758-71 B-2 (Lot # RT-0904) Submitted to NAWC

PEEL STRENGTH	**REQUIREMENT**		**RESULT (psiw/failure type)**
Substrate	**AMS-3265**	**MIL-PRF-81733**	
23377 on Anodized Al		20/100% cohesive	57/100% co
@ 48Hr 83282		20/100% cohesive	44/100% co
@ 48Hr 23699		20/100% cohesive	40/100% co
@ 48Hr JRF		20/100% cohesive	19/100% co
@ 48Hr 3% SaltWater		20/100% cohesive	70/100% co
IM6/3501-6		20/100% cohesive	56/100% co
@ 48Hr 83282		20/100% cohesive	37/100% co
@ 48Hr 23699		20/100% cohesive	53/100% co
@ 48Hr JRF		20/100% cohesive	25/100% co
@ 48Hr 3% SaltWater		20/100% cohesive	66/100% co
Alodined Al		20/100% cohesive	75/100% co
@ 48Hr 83282		20/100% cohesive	58/100% co
@ 48Hr 23699		20/100% cohesive	55/100% co
@ 48Hr JRF		20/100% cohesive	30/100% co
@ 48Hr 3% SaltWater		20/100% cohesive	69/50% Adhesive
IM7/5250-4	20/100% cohesive		82/100% co
85582 on Anodized Al	20/100% cohesive		69/100% co